Electronic Supplementary Material (ESI) for CrystEngComm.

Correlation of Solid-State Order to Optoelectronic Behavior in Heterocyclic Oligomers

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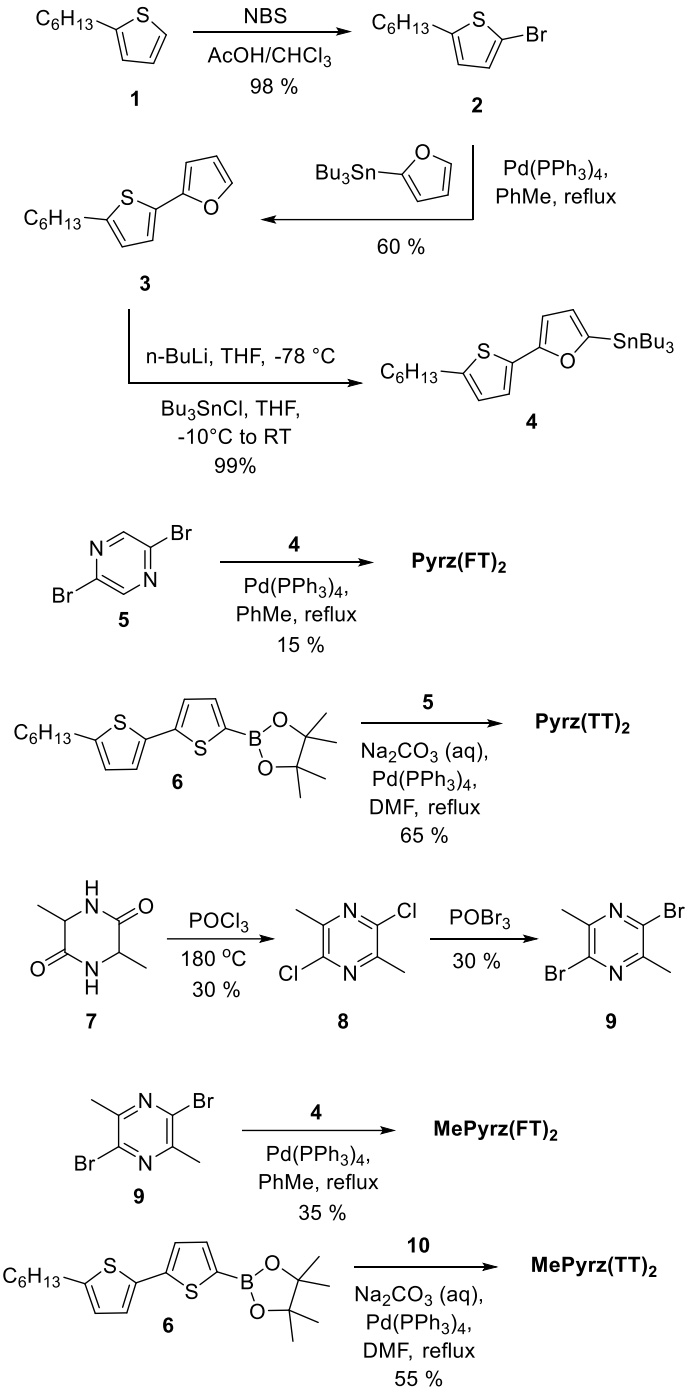
General Summary: Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. Tetrahydrofuran (THF), dichloromethane (DCM), and dimethylformamide (DMF) were degassed in 20 L drums and passed through two sequential purification columns (activated alumina; molecular sieves for DMF) under a positive argon atmosphere. Thin-layer chromatography (TLC) was performed on SiO_2-60 F254 aluminum plates with visualization by ultraviolet (UV) light or staining. Flash column chromatography was performed using Purasil SiO_2-60, 230–400 mesh from Whatman.1H NMR and 13C NMR spectra were recorded on a Bruker Avance-300 (300 MHz), Bruker Avance DRX-500 (500 MHz spectrometer) and were reported in ppm using solvent as an internal standard (CDCl3 at 7.26 ppm for 1H NMR and 77.15 ppm for 13C NMR). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration.



Scheme 1. Synthesis of heterocyclic oligomers.

Synthetic Details: Reported below are the full synthetic details for the preparation of $Pyrz(FT)_2$, $Pyrz(TT)_2$, $MePyrz(FT)_2$, and $MePyrz(TT)_2$.

2-Bromo-5-hexylthiophene (2) To N-Bromosuccinimide (4.65 g, 26.15 mmol) $CHCl_3$/Acetic acid (30 mL: 15 mL) was added and chilled in an ice bath for 15 minutes. 2-Hexylthiophene (1) (4.01 g, 23.83 mmol) was added and chilled for 15 minutes. The mixture was gradually heated up to 50 °C and refluxed for 30 minutes. The mixture was then cooled to room temperature. After 90 minutes, the mixture was quenched with Na_2HCO_3 (100 mL), extracted with $CHCl_3$ (100 mL) and the organic layer was dried over Na_2SO_4 and evaporated under vacuum. Yellow color solution (5.76 g, 23.39 mmol, yield = 98%). ^{1}H NMR: ($CDCl_3$, 500 MHz) δ 6.84 (d, J = 3.6 Hz, 1H), δ 6.53 (d, J = 3.5 Hz, 1H), δ 2.74 (t, J = 7.7 Hz, 2H), δ 1.62 (p, J = 7.5 Hz, 2H), δ 1.41 – δ 1.17 (m, 6H), δ 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR: ($CDCl_3$, 500 MHz) δ 147.72, 129.46, 124.42, 108.66, 31.64, 31.54, 30.54, 30.45, 28.78, 22.69, 14.19.

2-(5-Hexyl-2-thienyl)-furan (3) To 2-Bromo-5-hexylthiophene (2) (5.61 g, 22.84 mmol), $Pd(PPh_3)_4$ (1.64 g, 1.42 mmol) and dry toluene (150 mL) were added and stirred for 20 minutes. 2-(Tributylstannyl)furan (8.7 mL, 27.63 mmol) was added dropwise. The mixture was gradually heated up to 120 °C and refluxed overnight. The mixture was then cooled to room temperature. The reaction mixture was quenched with DI water and extracted with diethyl ether. The mixture was filtered through an activated carbon layer and dried over Na_2SO_4. The crude product was purified using column chromatography (Eluent: Hexane). Yellow color solution. (3.14 g, 59.88 mmol, yield = 60%) ^{1}H NMR: ($CDCl_3$, 500 MHz) δ 7.37 (d, *J* = 2.1 Hz, 1H), δ 7.05 (d, *J* = 3.5 Hz, 1H), δ 6.69 (d, *J* = 3.5 Hz, 1H), δ 6.44-6.37 (m, 2H), δ 2.80 (t, *J* = 7.6 Hz, 2H), δ 1.66 (p, *J* = 7.6 Hz, 2H), δ 1.43 – 1.26 (m, 6H), δ 0.90 (t, *J* = 5.4 Hz, 3H).

Tributyl(5-(5-hexylthiophen-2-yl)-furan-2-yl)-stannane (4) To the solution of 2-(5-Hexyl-2-thienyl)-furan (3) (2.5 g, 10.67 mmol), tetrahydrofuran (60 mL) was added and kept in an ice bath (-78 °C). Then n-Butyllithium (5.5 mL, 13.87 mmol) was added dropwise. Set up was covered using Al foil. After stirring at -78 °C for 1 hour, the mixture was warmed up to -10 °C. Tributyltin chloride (3.2 mL, 11.74 mmol) was added dropwise. The reaction mixture was kept overnight to warm up to room temperature. The reaction mixture was quenched with DI water (50 mL), extracted with Diethyl ether and the organic layer was dried over Na_2SO_4 and evaporated under vacuum. Orange color solution (5.6 g, 10.67 mmol, yield = 99%). ^{1}H NMR: ($CDCl_3$, 500 MHz) δ 7.03 (d, *J* = 3.6 Hz, 1H), δ 6.68 (d, *J* = 3.7 Hz, 1H), δ 6.55 (d, *J* = 3.2 Hz, 1H), δ 6.43 (d, *J* = 3.3 Hz, 1H).

2,5-Bis(5-(5-hexylthiophen-2-yl)-furan-2-yl)-pyrazine (Pyrz(FT)$_2$), Under nitrogen, to a three-neck round bottom flask, Tributyl(5-(5-hexylthiophen-2-yl)-furan-2-yl)-stannane (4) (5.6 g, 10.67 mmol) 2,5-Dibromopyrazine (5) (1.65 g, 6.94 mmol) and $Pd(PPh_3)_4$ (0.74 g/ 0.64 mmol) was added. Dry Toluene (75 mL) was added via a syringe. The reaction was done under reflux at 120 °C for 24 hrs. The reaction mixture was quenched with aqueous $NaHCO_3$. The product was extracted with $CHCl_3$. The organic layer then mixed with DI water and extracted 3 times and filtered through Celite. The organic layer was dried over anhydrous Na_2SO_4 and filtered under vacuum filtration. The organic layer was roto-evaporated. An orange color solid was obtained. To the solid product, Toluene (5 mL) and Hexane (20 mL) were added and placed, and ultra-sonicated to dissolve. Then another 10 ml of Hexane was added and filtered. Then, the filtrate was again subjected to filtration. The precipitate was taken and purified by column chromatography. (Eluent: Acetone: Hexane 1:4) Orange color solid ^{1}H NMR: ($CDCl_3$, 500 MHz) δ 8.92 (s, 2H), δ 7.22 (d, J = 3.6 Hz, 2H), δ 7.16 (d, *J* = 3.5 Hz, 2H), δ 6.76 (d, *J* = 3.5 Hz, 2H), δ 6.59 (d, *J* = 3.6 Hz, 2H), δ 2.83 (t, *J* = 7.6 Hz, 4H), δ 1.75 – 1.64 (m, 4H), δ 1.46 – 1.11 (m, 12H), δ 0.90 (t, 6H) ^{13}C NMR: ($CDCl_3$, 500 MHz) δ 151.47, 150.15, 146.68, 141.94, 139.50, 130.41, 125.06, 123.16, 112.66, 107.14, 31.70, 28.88, 28.44, 22.72, 14.23.

2,5-Bis(5'-hexyl-[2,2'-bithiophen]-5-yl)pyrazine (Pyrz(TT)$_2$), Under nitrogen, to a three neck round bottom flask, 2-(5'-hexyl-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) (1.51 g, 4.01 mmol), 2,5-Dibromopyrazine (5) (0.58 g, 2.43 mmol), $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol), Na_2CO_3 (0.45 g, 4.25 mmol) and H_2O (2.3 mL) was added and stirred for 10 minutes. Then Dimethylformamide (25 mL) was added and gradually heated up to 110 °C and refluxed for 24 hours. The reaction mixture was quenched with deionized water (50 mL) and extracted with chloroform three times and organic layer was separated. Orange color solid was floated on the surface of the organic layer. It was filtered. Light orange solid (0.68 g, 1.18 mmol, yield = 60%) ($CDCl_3$, 500 MHz) δ 8.81 (s, 2H), δ 7.54 (d, J = 3.9 Hz, 2H), δ 7.13 (d, *J* = 3.9 Hz, 2H), δ 7.09 (d, *J* = 3.6 Hz, 2H), δ 6.72 (d, *J* = 3.6 Hz, 2H), δ 2.81 (t, *J* = 7.6 Hz, 4H), δ 1.69 (p, *J* = 7.6 Hz, 4H), δ 1.45 – 1.28 (m, 12H), δ 0.90 (t, 6H) ^{13}C NMR: ($CDCl_3$, 500 MHz) δ 146.70, 145.69, 141.29, 139.36, 139.34, 134.54, 126.06, 125.22, 124.39, 124.16, 31.72, 30.39, 28.92, 22.73, 14.24.

2,5-bis(5-(5-hexylthiophen-2-yl)furan-2-yl)-3,6-dimethylpyrazine (MePyrz(FT)$_2$) Under nitrogen, to a round bottom flask, Tributyl(5-(5-hexylthiophen-2-yl)-furan-2-yl)-stannane (4) (1.04 g, 2.0 mmol) 2,5-dibromo-3,6-dimethylpyrazine (10) (300 mg, 1.12 mmol) and $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) was added. Dry Toluene (15 mL) was added via a syringe. The reaction was done under reflux at 120 °C for 24 hrs. The reaction mixture was quenched with aqueous $NaHCO_3$. The product was extracted with $CHCl_3$. The organic layer then mixed with DI water and extracted 3 times and filtered through Celite. The organic layer was dried over anhydrous Na_2SO_4 and filtered under vacuum filtration. The organic layer was evaporated under vacuum. An orange color solid was obtained. The solid was purified by column chromatography. (Eluent: Ethyl acetate: Hexane 1:20) Orange color solid. (0.20 g, 0.33 mmol, yield = 35%) ^{1}H NMR (300 MHz, CDCl3) δ 7.22 – 7.16 (m, 4H), 6.75 (d, J = 3.6 Hz, 2H), 6.60 (d, J = 3.6 Hz, 2H), 2.90 (s, 6H), 2.83 (t, J = 7.6 Hz, 4H), 1.71 (p, J = 7.5 Hz, 4H), 1.37 – 1.15 (m, 12H), 0.91 (t, 6H).

2,5-Bis(5'-hexyl-[2,2'-bithiophen]-5-yl)-3,6-dimethylpyrazine (MePyrz(TT)$_2$) Under nitrogen, to a round bottom flask, 2-(5'-hexyl-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) (388 mg, 1.02 mmol), 2,5-dibromo-3,6-dimethylpyrazine (10) (150 mg, 0.56 mmol), $Pd(PPh_3)_4$ (120 mg, 0.10 mmol), Na_2CO_3 (113 mg, 1.07 mmol) and H_2O (0.6 mL) was added and stirred for 10 minutes. Then dry dimethylformamide (6 mL) was added and gradually heated up to 110 °C and refluxed for 24 hours. The reaction mixture was quenched with deionized water (50 mL) and extracted with chloroform three times and organic layer was separated. Orange color solid was floated on the surface of the organic layer. solid was filtered. Orange solid (170 mg, 0.28 mmol, yield = 55%) ^{1}H NMR (300 MHz, CDCl3) δ 7.45 (d, J = 4.0 Hz, 2H), 7.14 (d, J = 4.0 Hz, 2H), 7.10 (d, J = 3.6 Hz, 2H), 6.72 (d, J = 3.6 Hz, 2H), 2.94 – 2.63 (m, 10H), 1.70 (p, J = 7.4 Hz, 4H), 1.40 – 1.20 (m, 12H), 0.89 (t, 6H).

^{1}H and ^{13}C NMR Spectra

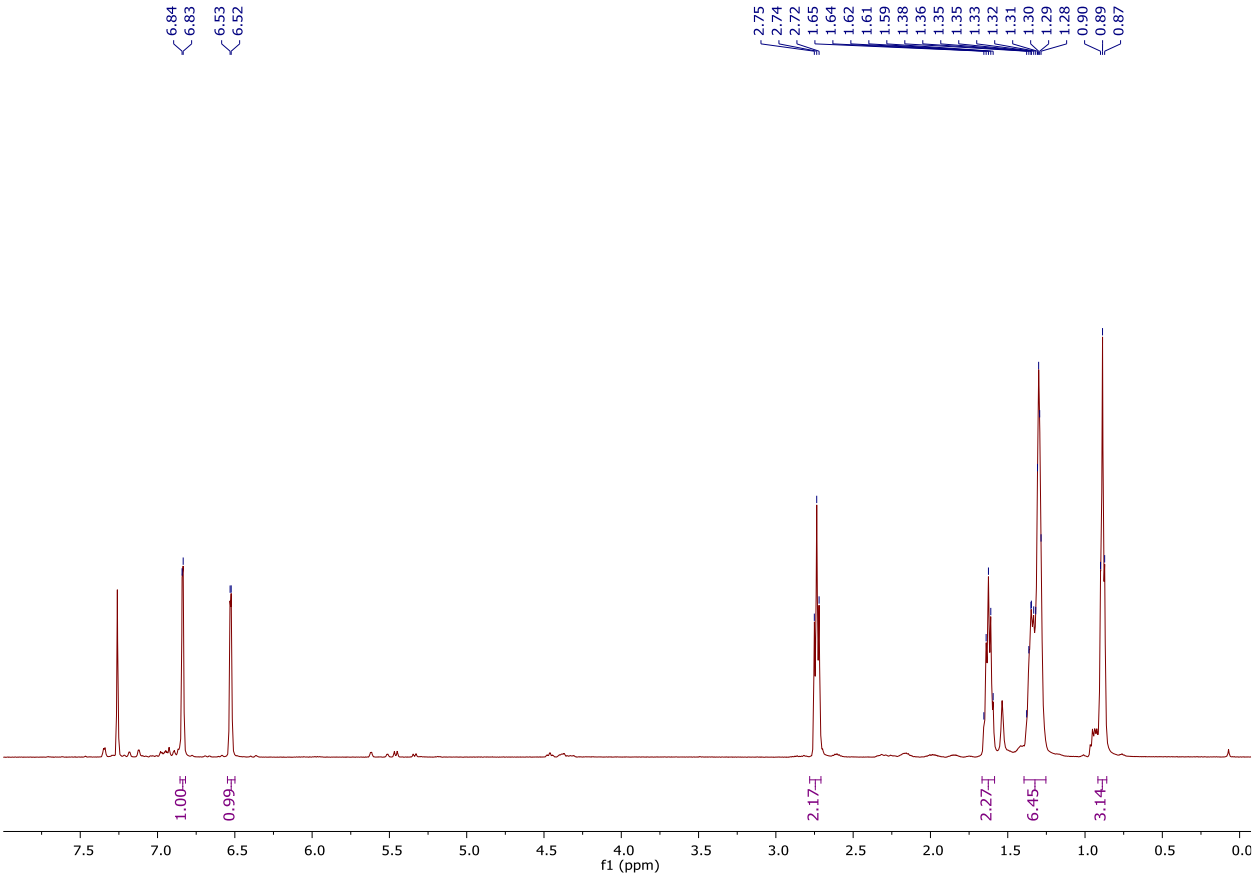


Figure S1. ^{1}H NMR Spectrum of compound **2** ($CDCl_3$, 500 Hz)

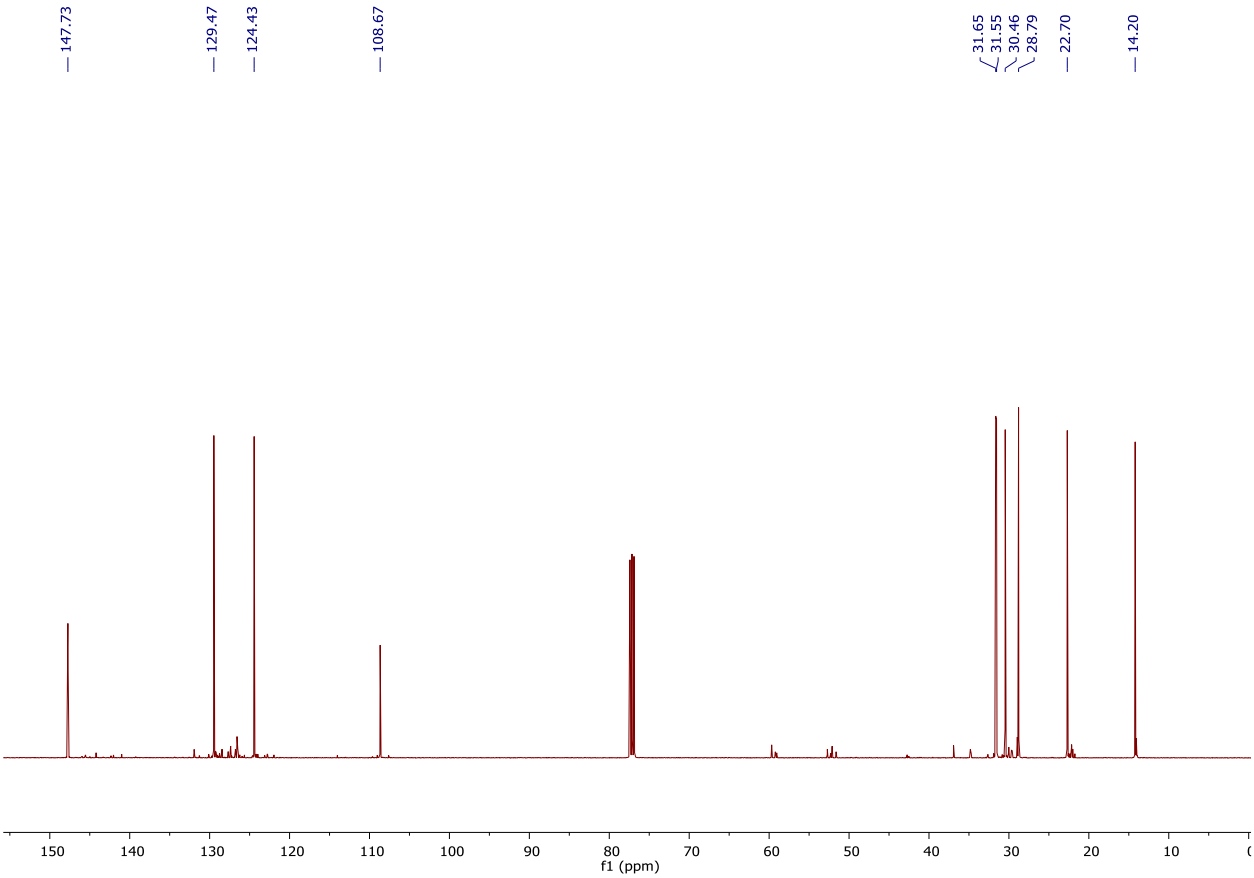


Figure S2. ^{13}C NMR spectrum of compound **2** ($CDCl_3$, 500 Hz)

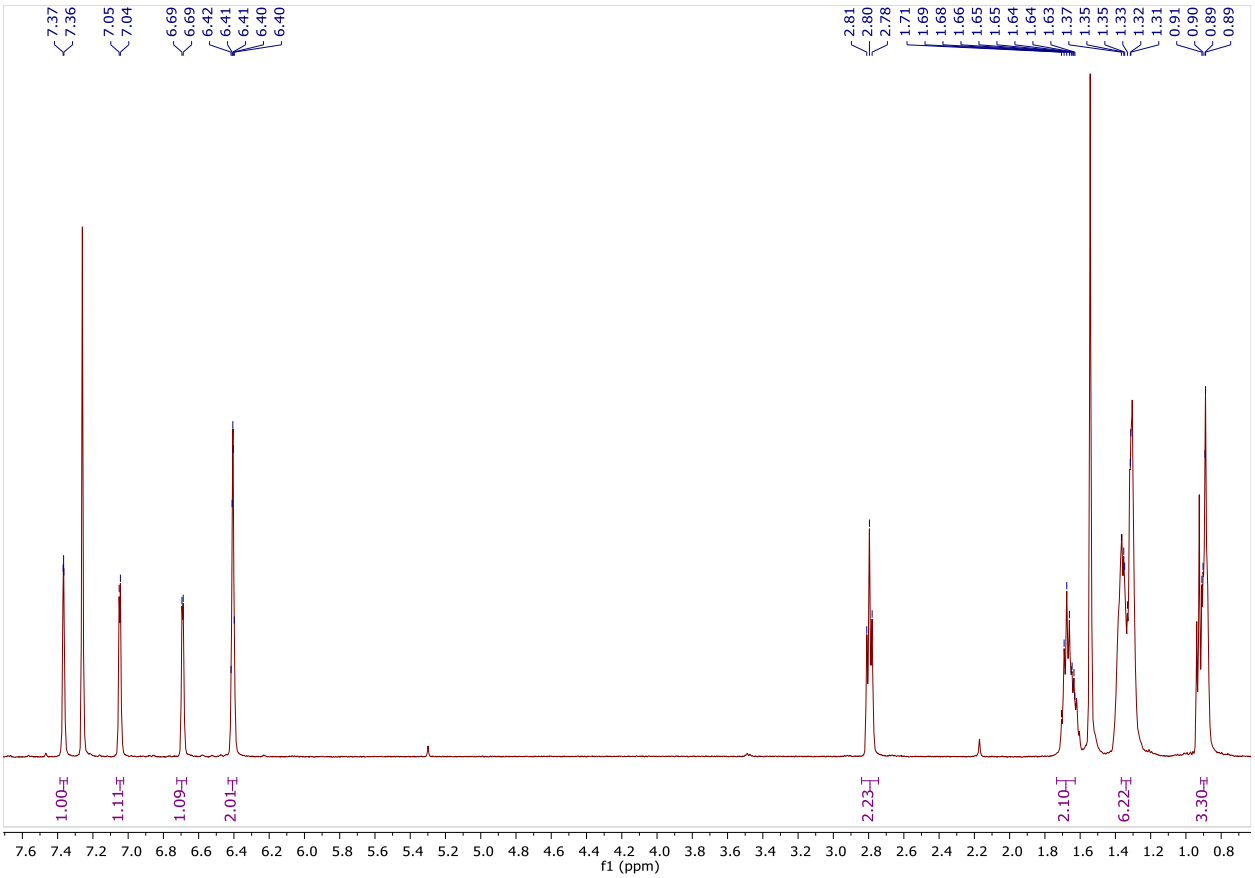


Figure S3. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 500 Hz)

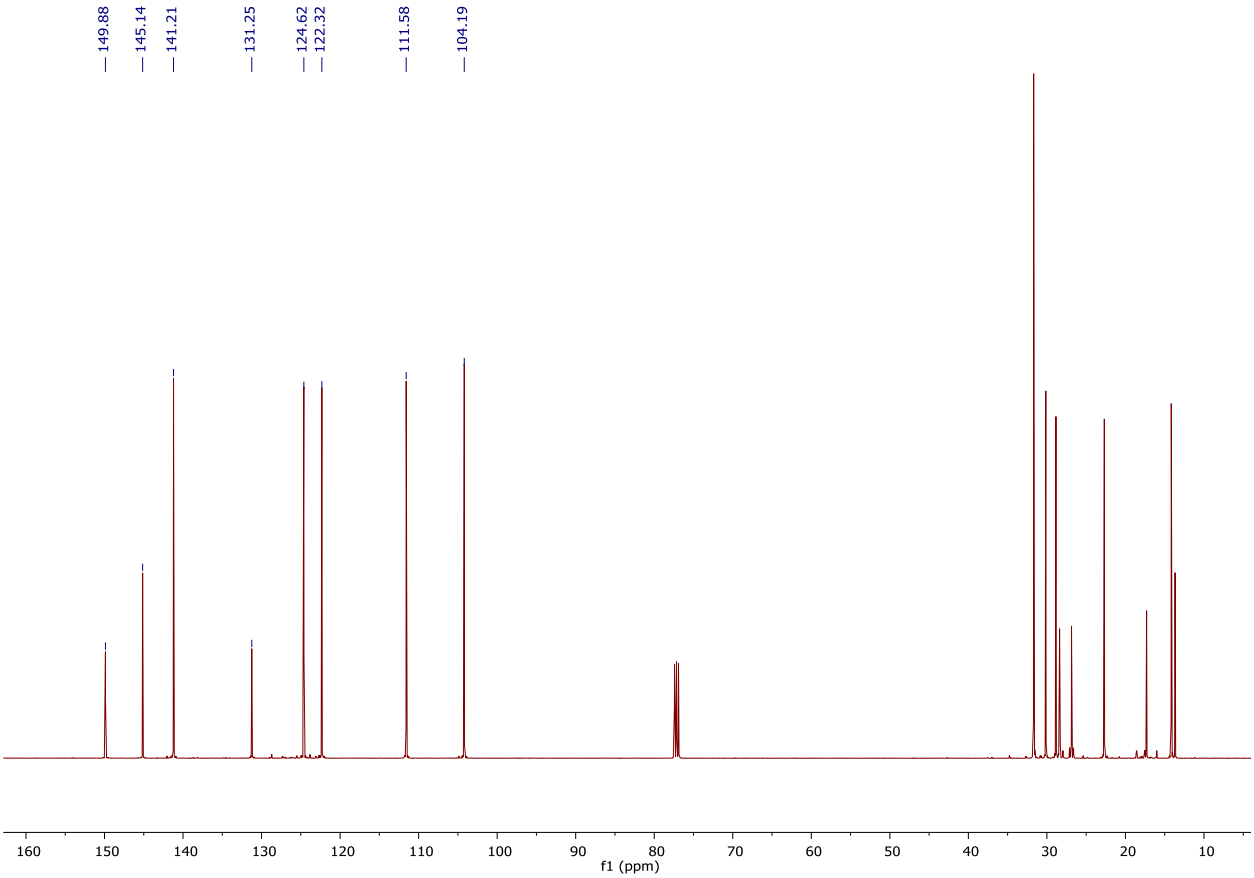


Figure S4. ^{13}C NMR spectrum of compound **3** ($CDCl_3$, 500 Hz)

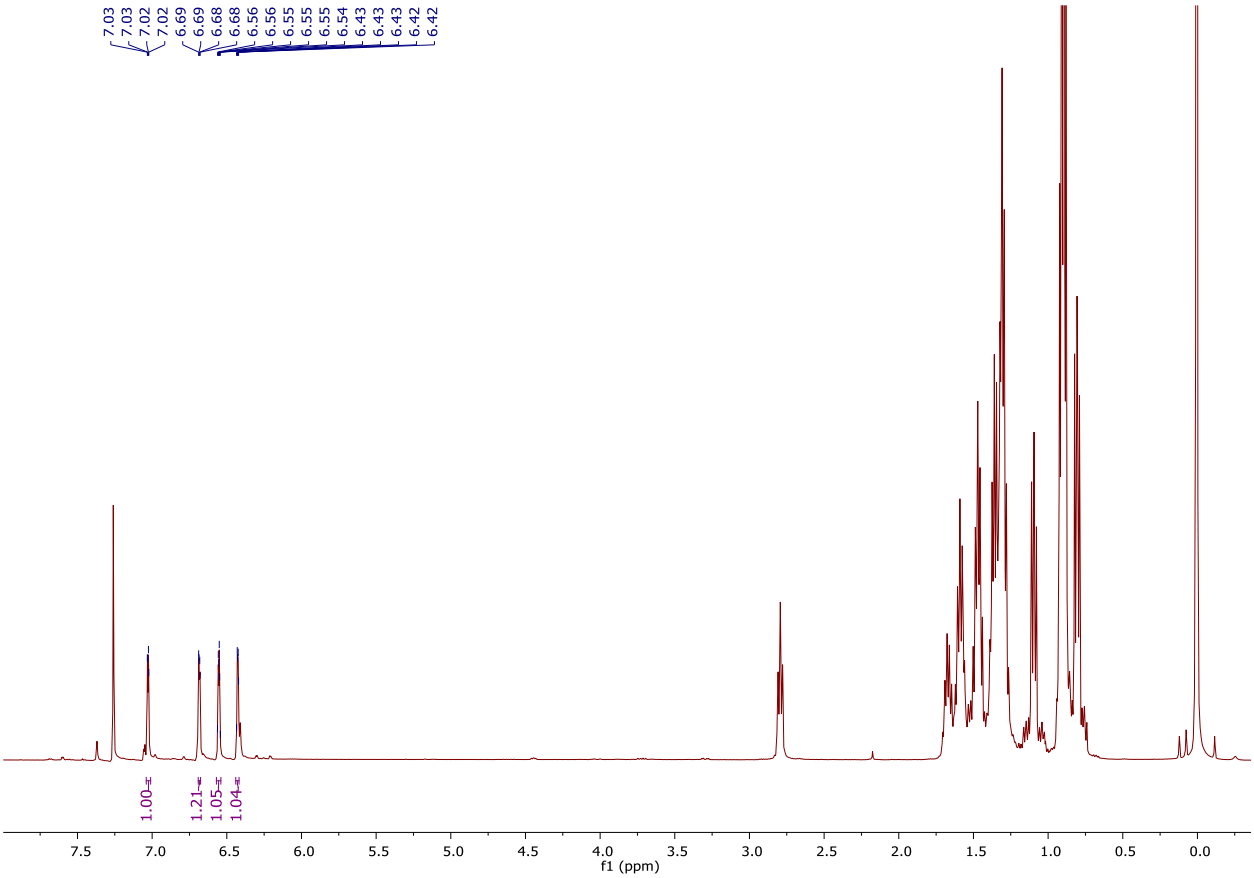


Figure S5. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 500 Hz)

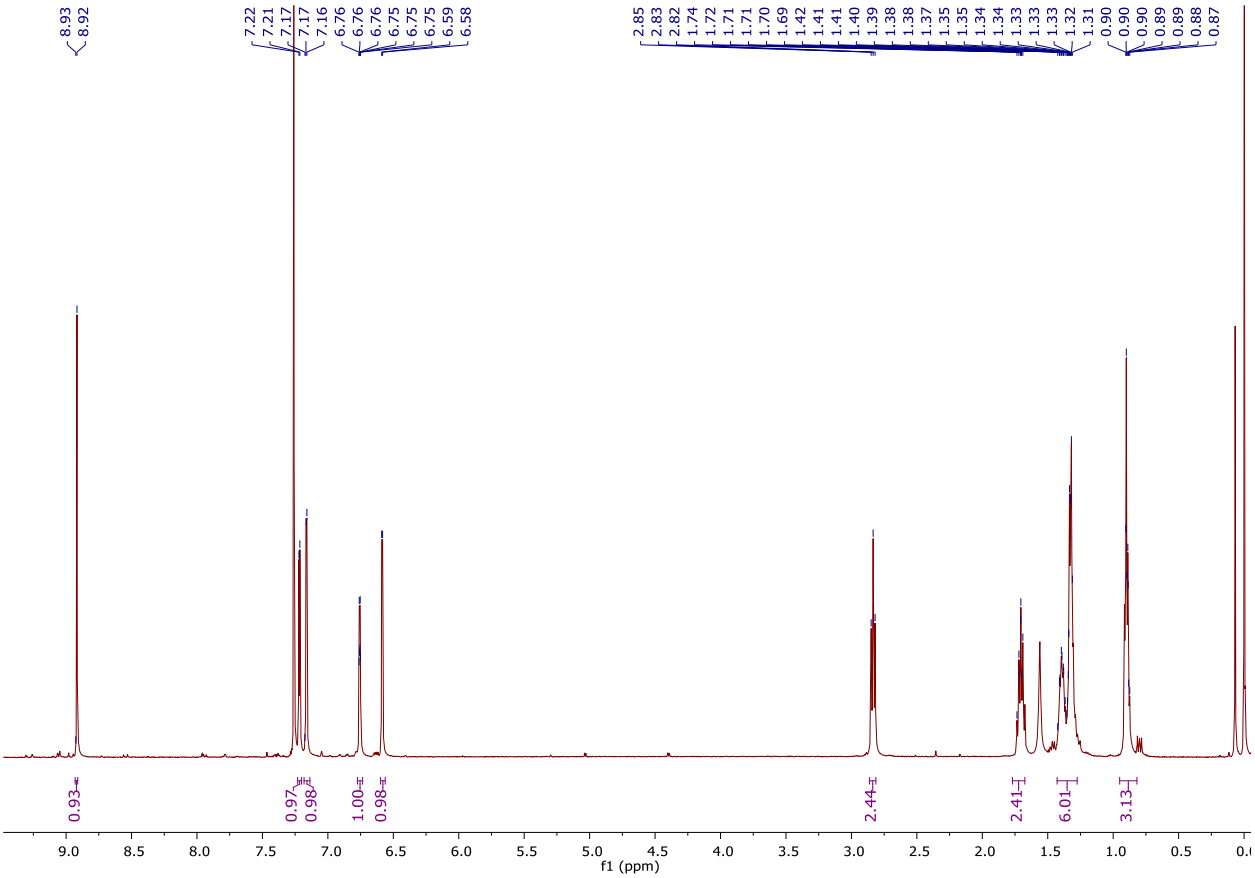


Figure S6. ^{1}H NMR spectrum of compound **Pyrz(FT)$_2$** ($CDCl_3$, 500 Hz)

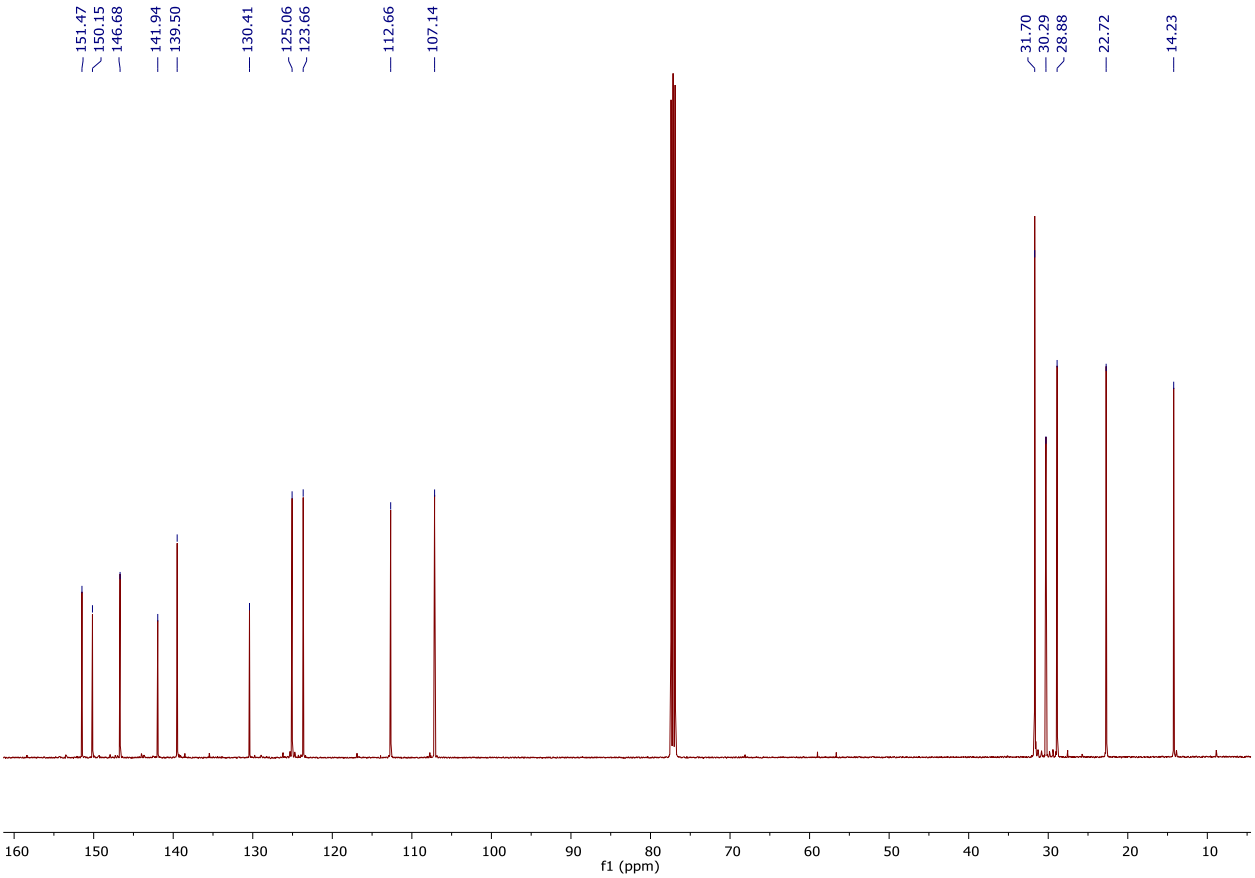


Figure S7. ^{13}C NMR spectrum of compound **Pyrz(FT)$_2$** ($CDCl_3$, 500 Hz)

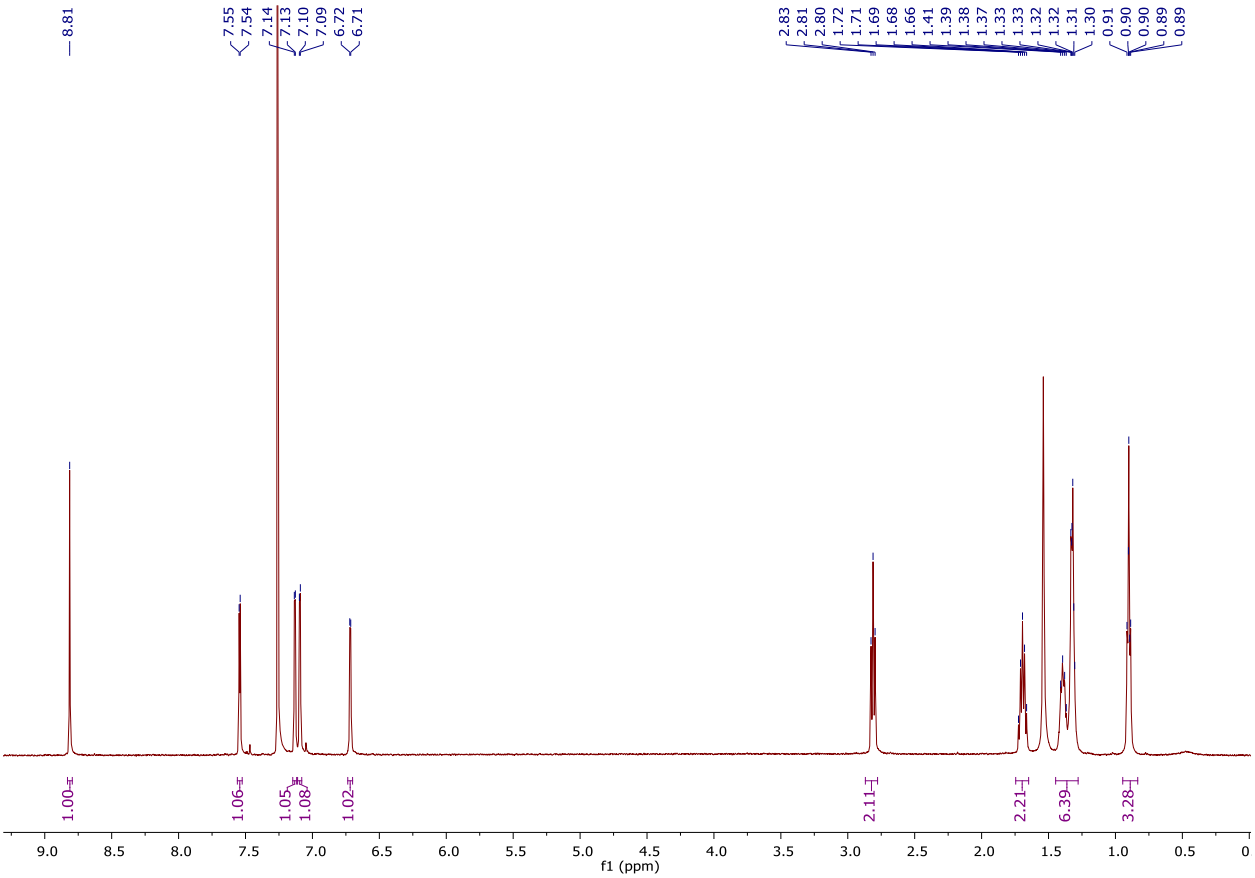


Figure S8. ^{1}H NMR spectrum of compound **Pyrz(TT)$_2$** ($CDCl_3$, 500 Hz)

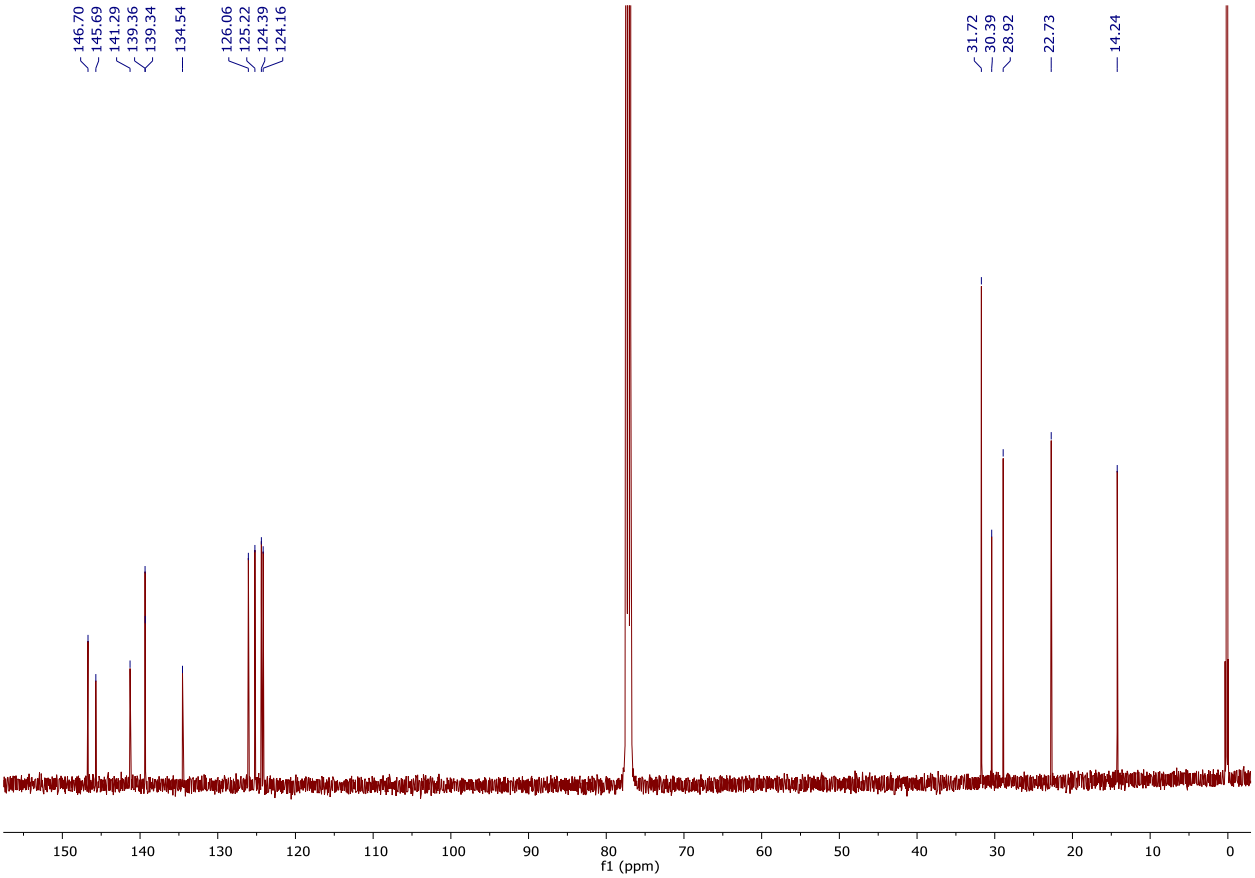


Figure S9. ^{13}C NMR spectrum of compound **Pyrz(TT)$_2$** ($CDCl_3$, 500 Hz)

Figure 1

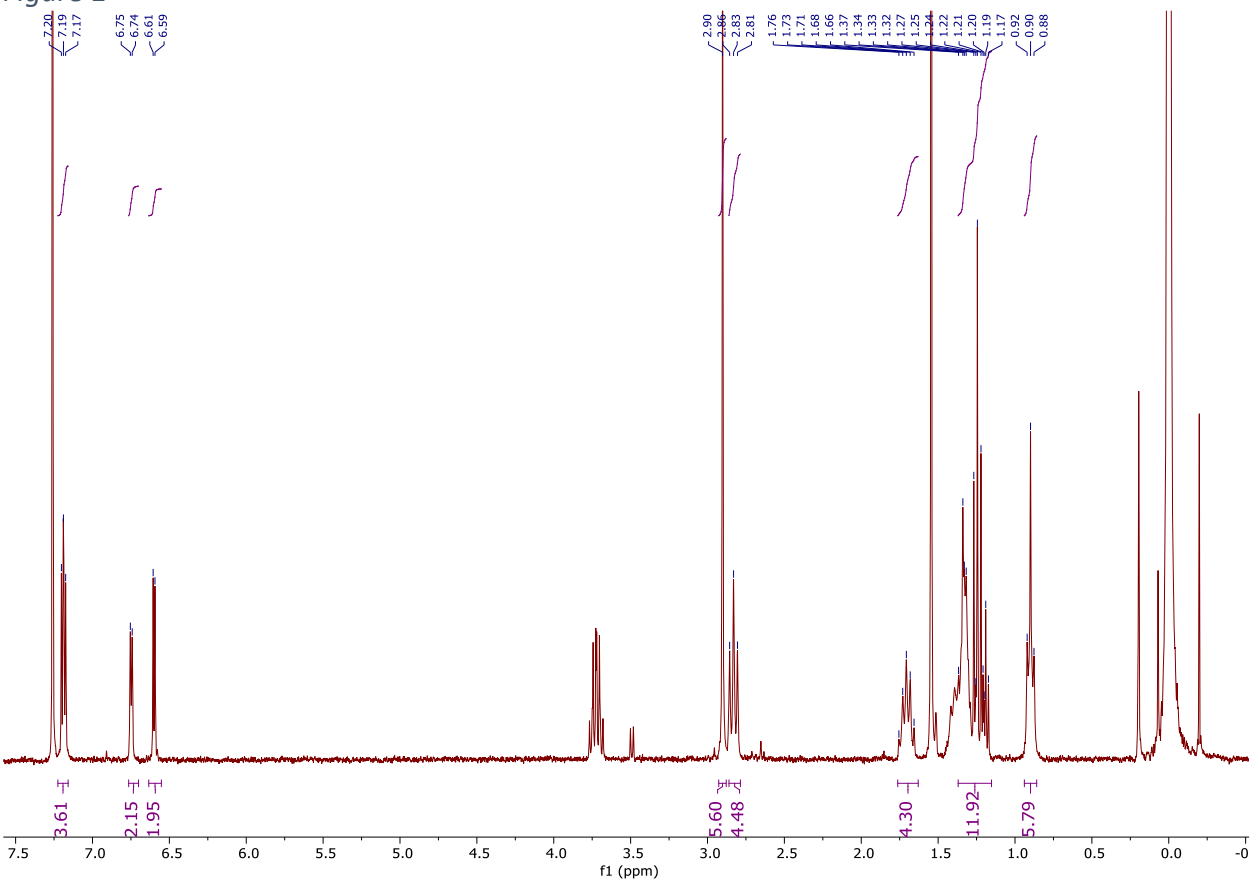


Figure S10. ^{1}H NMR spectrum of compound **MePyrz(FT)$_2$** ($CDCl_3$, 300 Hz)

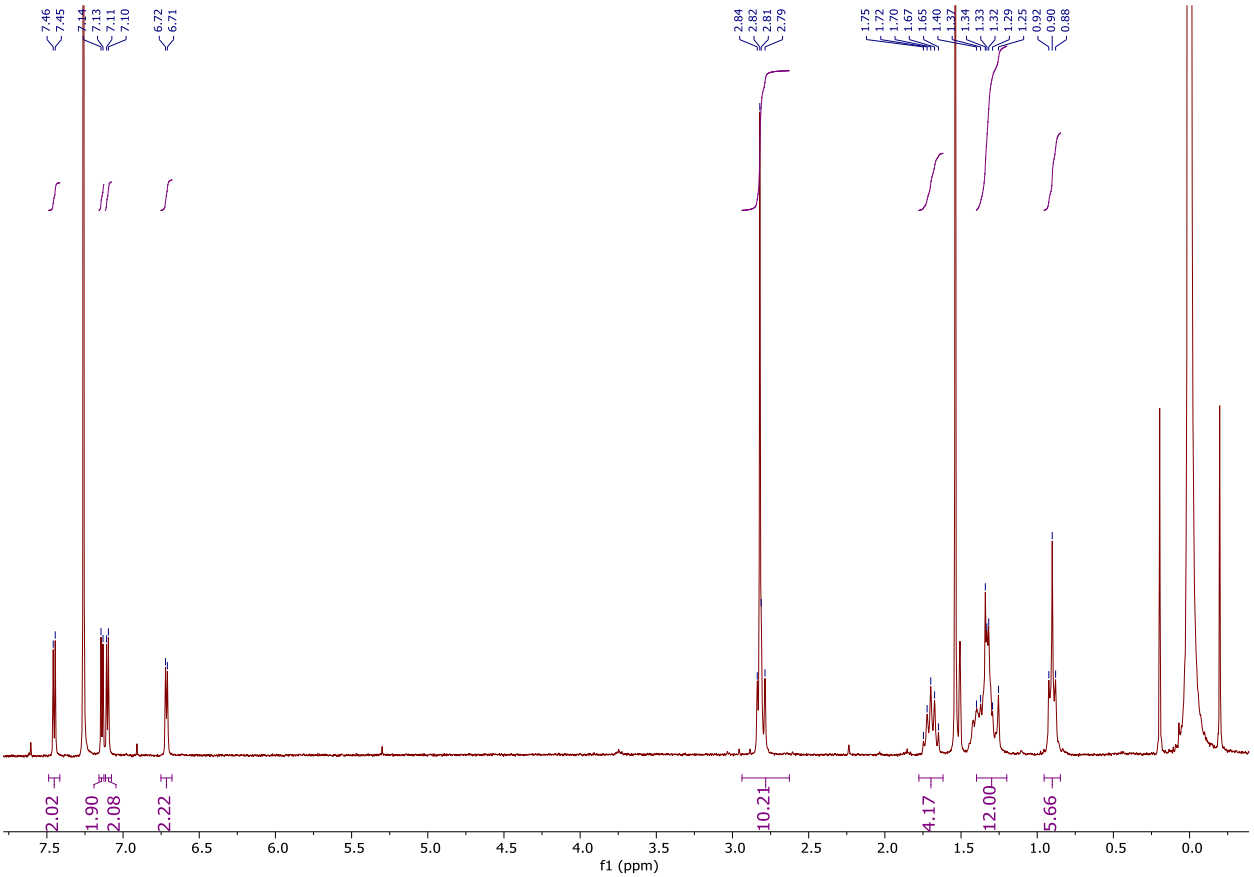


Figure S11. ^{1}H NMR spectrum of compound **MePyrz(TT)$_2$** ($CDCl_3$, 300 Hz)

Cyclic voltammogram

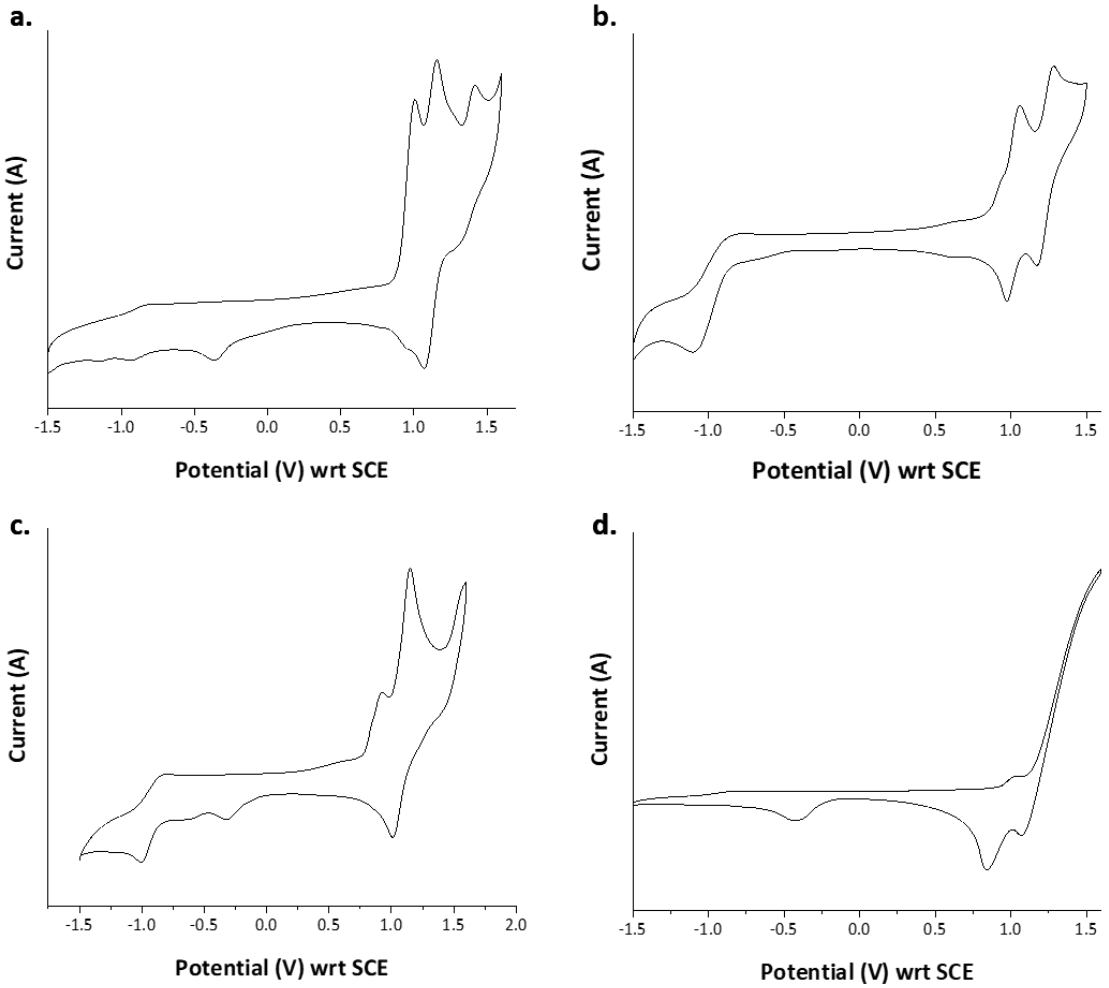


Figure S12. Cyclic voltammograms of 1 mM (a) **Pyrz(FT)$_2$** (b) **Pyrz(TT)$_2$** (c) **MePyrz(FT)$_2$** (d) **MePyrz(TT)$_2$** in DCM with 0.10 mol dm-3 tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF^{6-}$) as the background electrolyte.

Computational Details and Results

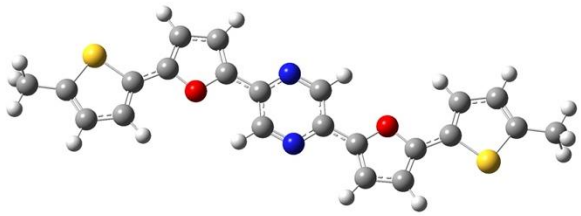


Figure S13. Optimized S_0 geometry of Pyrz(FT)$_2$ with C_{2h} symmetry.

Table S1. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_0 geometry of Pyrz(FT)$_2$ with C_{2h} symmetry.

C	4.468210	0.000000	6.005278
C	3.128811	0.000000	6.301424
S	2.892154	0.000000	8.028854
C	4.603991	0.000000	8.333787
C	5.293989	0.000000	7.156000
C	2.016765	0.000000	5.394455
O	2.305293	0.000000	4.060545
C	1.117090	0.000000	3.380132
C	0.080822	0.000000	4.272024
C	0.656052	0.000000	5.564451
C	1.159265	0.000000	1.938011
N	-0.018589	0.000000	1.289859
C	0.013397	0.000000	-0.030084
C	1.217594	0.000000	-0.754123
N	2.395448	0.000000	-0.105971
C	2.363462	0.000000	1.213973
C	1.259769	0.000000	-2.196243
O	0.071566	0.000000	-2.876656
C	0.360094	0.000000	-4.210567
C	1.720807	0.000000	-4.380563
C	2.296037	0.000000	-3.088136
C	-0.751952	0.000000	-5.117535
S	-0.515296	0.000000	-6.844966
C	-2.227132	0.000000	-7.149899
C	-2.917130	0.000000	-5.972112
C	-2.091351	0.000000	-4.821390
H	2.240102	0.000000	-5.323282
H	0.136757	0.000000	6.507171

H	-2.462614	0.000000	-3.808354
H	4.839473	0.000000	4.992242
C	-2.765641	0.000000	-8.543833
C	5.142500	0.000000	9.727721
H	-3.997178	0.000000	-5.932122
H	6.374037	0.000000	7.116010
H	3.338391	0.000000	-2.825143
H	-0.961532	0.000000	4.009031
H	3.314112	0.000000	1.731596
H	-0.937253	0.000000	-0.547708
H	6.231426	0.000000	9.701458
H	-3.854567	0.000000	-8.517569
H	4.821404	0.879507	10.289389
H	4.821404	-0.879507	10.289389
H	-2.444545	0.879507	-9.105500
H	-2.444545	-0.879507	-9.105500

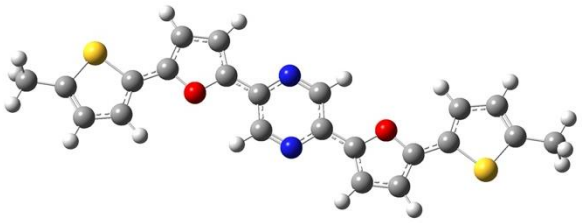


Figure S14. Optimized S_1 geometry of Pyrz(FT)$_2$ with C_{2h} symmetry.

Table S2. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_1 geometry of Pyrz(FT)$_2$ with C_{2h} symmetry.

C	4.490919	0.000000	6.008848
C	3.133187	0.000000	6.293430
S	2.882337	0.000000	8.027943
C	4.593605	0.000000	8.340529
C	5.296263	0.000000	7.161380
C	2.051199	0.000000	5.385463
O	2.351628	0.000000	4.045060
C	1.165993	0.000000	3.355384
C	0.109881	0.000000	4.261792
C	0.671512	0.000000	5.538947
C	1.185876	0.000000	1.938473
N	-0.035048	0.000000	1.308298
C	-0.006592	0.000000	-0.002144
C	1.190983	0.000000	-0.754584
N	2.411907	0.000000	-0.124409
C	2.383451	0.000000	1.186033
C	1.210866	0.000000	-2.171495
O	0.025231	0.000000	-2.861171
C	0.325660	0.000000	-4.201575
C	1.705346	0.000000	-4.355059
C	2.266978	0.000000	-3.077903
C	-0.756328	0.000000	-5.109541
S	-0.505478	0.000000	-6.844055
C	-2.216746	0.000000	-7.156640
C	-2.919404	0.000000	-5.977492
C	-2.114060	0.000000	-4.824960
H	2.227717	0.000000	-5.296647
H	0.149142	0.000000	6.480536
H	-2.492080	0.000000	-3.814722
H	4.868939	0.000000	4.998610
C	-2.747432	0.000000	-8.550449

C	5.124291	0.000000	9.734337
H	-4.000073	0.000000	-5.951412
H	6.376932	0.000000	7.135301
H	3.305565	0.000000	-2.801588
H	-0.928707	0.000000	3.985477
H	3.337342	0.000000	1.701202
H	-0.960483	0.000000	-0.517314
H	6.213350	0.000000	9.715899
H	-3.836492	0.000000	-8.532011
H	4.798105	0.878926	10.295927
H	4.798105	-0.878926	10.295927
H	-2.421246	0.878926	-9.112038
H	-2.421246	-0.878926	-9.112038

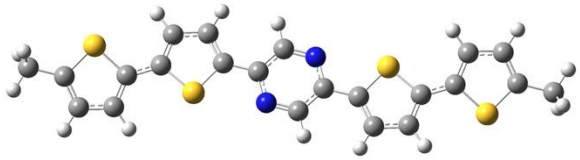


Figure S15. Optimized S_0 geometry of Pyrz(TT)$_2$ with C_i symmetry.

Table S3. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_0 geometry of Pyrz(TT)$_2$ with C_i symmetry.

S	-1.001267	-7.948031	-0.087761
C	0.102680	-6.596784	0.014944
C	1.393571	-7.057035	0.078762
C	1.494313	-8.469289	0.052903
C	0.290598	-9.107855	-0.029666
C	-0.380104	-5.236924	0.019792
S	0.694209	-3.902043	-0.289524
C	-0.591363	-2.744016	-0.092780
C	-1.778280	-3.382156	0.182439
C	-1.660915	-4.782755	0.246493
C	-0.308534	-1.330122	-0.231937
N	0.958817	-0.971942	-0.503809
C	1.229418	0.312871	-0.634709
C	0.248095	1.308671	-0.501108
N	-1.019256	0.950491	-0.229236
C	-1.289857	-0.334322	-0.098336
C	0.530924	2.722565	-0.640265
S	-0.754648	3.880592	-0.443521
C	0.319665	5.215473	-0.752837
C	1.600476	4.761304	-0.979538
C	1.717841	3.360705	-0.915484
C	-0.163119	6.575333	-0.747989
C	-1.454010	7.035584	-0.811807
C	-1.554752	8.447838	-0.785948
C	-0.351037	9.086404	-0.703378
S	0.940828	7.926580	-0.645284
C	-0.079919	10.555486	-0.661658
C	0.019480	-10.576937	-0.071387
H	2.426629	5.420044	-1.203452
H	-2.487068	-5.441495	0.470408

H	-2.306392	6.376914	-0.892658
H	2.245953	-6.398365	0.159613
H	-2.493836	8.980722	-0.833435
H	2.433397	-9.002173	0.100390
H	2.649698	2.839397	-1.075560
H	-2.710137	-2.860848	0.342515
H	-2.319135	-0.592035	0.119855
H	2.258696	0.570584	-0.852900
H	-1.020076	11.104644	-0.694771
H	0.959637	-11.126095	-0.038274
H	0.446383	10.847747	0.249171
H	0.528405	10.882055	-1.507487
H	-0.588844	-10.903505	0.774442
H	-0.506822	-10.869198	-0.982216

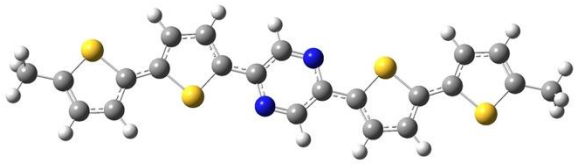


Figure S16. Optimized S_1 geometry of Pyrz(TT)$_2$ with C_{2h} symmetry.

Table S4. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_1 geometry of Pyrz(TT)$_2$ with C_{2h} symmetry.

S	-0.975810	-7.925900	0.000000
C	0.126135	-6.555742	0.000000
C	1.434716	-7.016702	0.000000
C	1.538051	-8.418701	0.000000
C	0.330370	-9.071019	0.000000
C	-0.349939	-5.219064	0.000000
S	0.753621	-3.857566	0.000000
C	-0.575538	-2.716268	0.000000
C	-1.802303	-3.390734	0.000000
C	-1.674265	-4.771653	0.000000
C	-0.290563	-1.325936	0.000000
N	1.028550	-0.956544	0.000000
C	1.292768	0.325872	0.000000
C	0.290563	1.325936	0.000000
N	-1.028550	0.956544	0.000000
C	-1.292768	-0.325872	0.000000
C	0.575538	2.716268	0.000000
S	-0.753621	3.857566	0.000000
C	0.349939	5.219064	0.000000
C	1.674265	4.771653	0.000000
C	1.802303	3.390734	0.000000
C	-0.126135	6.555742	0.000000
C	-1.434716	7.016702	0.000000
C	-1.538051	8.418701	0.000000
C	-0.330370	9.071019	0.000000
S	0.975810	7.925900	0.000000
C	-0.074190	10.540415	0.000000
C	0.074190	-10.540415	0.000000
H	2.516074	5.448932	0.000000
H	-2.516074	-5.448932	0.000000

H	-2.285606	6.351621	0.000000
H	2.285606	-6.351621	0.000000
H	-2.480111	8.948784	0.000000
H	2.480111	-8.948784	0.000000
H	2.753589	2.881078	0.000000
H	-2.753589	-2.881078	0.000000
H	-2.340812	-0.605364	0.000000
H	2.340812	0.605364	0.000000
H	-1.019474	11.081596	0.000000
H	1.019474	-11.081596	0.000000
H	0.493458	10.855882	0.878852
H	0.493458	10.855882	-0.878852
H	-0.493458	-10.855882	0.878852
H	-0.493458	-10.855882	-0.878852

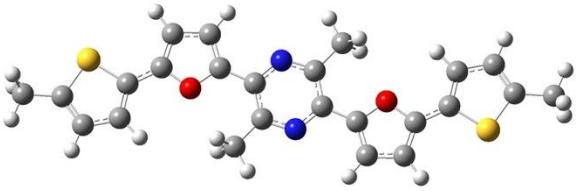


Figure S17. Optimized S_0 geometry of MePyrz(FT)$_2$ with C_{2h} symmetry.

Table S5. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_0 geometry of MePyrz(FT)$_2$ with C_{2h} symmetry.

C	4.512756	0.000000	6.112630
C	3.165147	0.000000	6.370100
S	2.879672	0.000000	8.090402
C	4.582458	0.000000	8.444365
C	5.305428	0.000000	7.286823
C	2.078541	0.000000	5.433002
O	2.404640	0.000000	4.108331
C	1.238384	0.000000	3.389566
C	0.177589	0.000000	4.256366
C	0.713690	0.000000	5.563444
C	1.271830	0.000000	1.941039
N	0.060235	0.000000	1.364494
C	-0.060660	0.000000	0.046100
C	1.105029	0.000000	-0.757151
N	2.316624	0.000000	-0.180606
C	2.437519	0.000000	1.137789
C	1.138475	0.000000	-2.205677
O	-0.027781	0.000000	-2.924443
C	0.298318	0.000000	-4.249114
C	1.663169	0.000000	-4.379556
C	2.199270	0.000000	-3.072478
C	-0.788288	0.000000	-5.186212
S	-0.502813	0.000000	-6.906514
C	-2.205599	0.000000	-7.260477
C	-2.928569	0.000000	-6.102935
C	-2.135897	0.000000	-4.928742
H	2.209989	0.000000	-5.306685
H	0.166870	0.000000	6.490574
H	-2.536554	0.000000	-3.926978
H	4.913413	0.000000	5.110867
C	-2.703852	0.000000	-8.669297

C	5.080711	0.000000	9.853186
H	-4.009370	0.000000	-6.093735
H	6.386229	0.000000	7.277623
H	3.233129	0.000000	-2.779943
H	-0.856270	0.000000	3.963832
H	6.169976	0.000000	9.858197
H	-3.793117	0.000000	-8.674309
H	4.743741	0.879499	10.405560
H	4.743741	-0.879499	10.405560
H	-2.366882	0.879499	-9.221671
H	-2.366882	-0.879499	-9.221671
C	3.842301	0.000000	1.674024
H	4.033011	0.874830	2.296070
H	4.033011	-0.874830	2.296070
H	4.531038	0.000000	0.833441
C	-1.465442	0.000000	-0.490136
H	-1.656152	0.874830	-1.112182
H	-1.656152	-0.874830	-1.112182
H	-2.154179	0.000000	0.350448

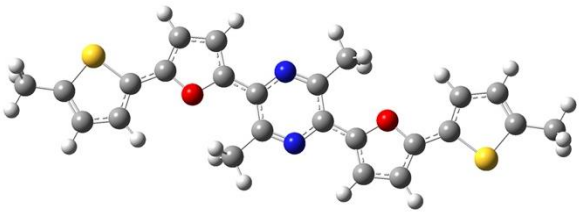


Figure S18. Optimized S_1 geometry of MePyrz(FT)$_2$ with C_{2h} symmetry.

Table S6. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_1 geometry of MePyrz(FT)$_2$ with C_{2h} symmetry.

C	4.532556	0.000000	6.115602
C	3.166883	0.000000	6.359640
S	2.865556	0.000000	8.086522
C	4.567350	0.000000	8.449635
C	5.303785	0.000000	7.291792
C	2.110472	0.000000	5.422184
O	2.448182	0.000000	4.090627
C	1.284487	0.000000	3.362925
C	0.203532	0.000000	4.245559
C	0.727193	0.000000	5.536283
C	1.296987	0.000000	1.942706
N	0.045832	0.000000	1.382956
C	-0.078864	0.000000	0.076364
C	1.079872	0.000000	-0.758818
N	2.331027	0.000000	-0.199068
C	2.455723	0.000000	1.107525
C	1.092372	0.000000	-2.179037
O	-0.071323	0.000000	-2.906739
C	0.266387	0.000000	-4.238296
C	1.649666	0.000000	-4.352395
C	2.173327	0.000000	-3.061671
C	-0.790024	0.000000	-5.175751
S	-0.488697	0.000000	-6.902634
C	-2.190491	0.000000	-7.265746
C	-2.926926	0.000000	-6.107904
C	-2.155697	0.000000	-4.931713
H	2.199110	0.000000	-5.278486
H	0.177749	0.000000	6.462375
H	-2.564320	0.000000	-3.933412
H	4.941179	0.000000	5.117301
C	-2.679564	0.000000	-8.674775

C	5.056423	0.000000	9.858663
H	-4.007966	0.000000	-6.113406
H	6.384825	0.000000	7.297295
H	3.203294	0.000000	-2.756815
H	-0.826435	0.000000	3.940703
H	6.145610	0.000000	9.872426
H	-3.768751	0.000000	-8.688537
H	4.714059	0.878942	10.410617
H	4.714059	-0.878942	10.410617
H	-2.337200	0.878942	-9.226729
H	-2.337200	-0.878942	-9.226729
C	3.862613	0.000000	1.638659
H	4.054294	0.874950	2.260758
H	4.054294	-0.874950	2.260758
H	4.547959	0.000000	0.795260
C	-1.485754	0.000000	-0.454770
H	-1.677435	0.874950	-1.076870
H	-1.677435	-0.874950	-1.076870
H	-2.171100	-0.000000	0.388628

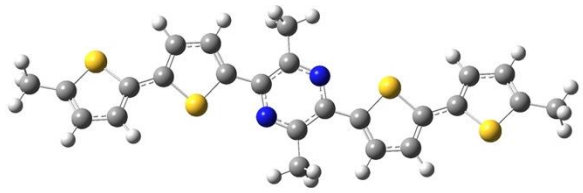


Figure S19. Optimized S_0 geometry of MePyrz(TT)$_2$ with C_i symmetry.

Table S7. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_0 geometry of MePyrz(TT)$_2$ with C_i symmetry.

C	-1.419173	6.977277	0.282488
C	-0.130905	6.559084	0.064035
S	0.891823	7.940966	-0.252912
C	-0.427443	9.056712	-0.073387
C	-1.581213	8.381954	0.203921
C	0.404128	5.218740	0.067645
S	-0.644120	3.832028	-0.007284
C	0.706729	2.722737	0.055194
C	1.890452	3.425782	0.116662
C	1.720790	4.823498	0.124160
C	0.400420	1.300839	0.030247
C	1.338513	0.241220	0.062372
N	0.908254	-1.009768	0.031242
C	-0.400421	-1.300839	-0.030249
C	-1.338513	-0.241220	-0.062374
N	-0.908254	1.009768	-0.031244
C	-0.706730	-2.722737	-0.055196
S	0.644120	-3.832028	0.007282
C	-0.404129	-5.218740	-0.067647
C	-1.720790	-4.823498	-0.124162
C	-1.890452	-3.425782	-0.116664
C	0.130905	-6.559084	-0.064037
C	1.419173	-6.977277	-0.282490
C	1.581212	-8.381954	-0.203923
C	0.427442	-9.056712	0.073386
S	-0.891824	-7.940966	0.252910
C	0.225966	-10.530130	0.221611
C	-0.225966	10.530130	-0.221613
H	2.543851	5.520380	0.187406
H	-2.543851	-5.520380	-0.187408
H	-2.224594	6.294301	0.509877

H	2.224594	-6.294301	-0.509879
H	-2.526628	8.883698	0.354328
H	2.526627	-8.883698	-0.354330
H	2.861302	2.965389	0.163093
H	-2.861303	-2.965389	-0.163095
H	-1.175426	11.047107	-0.087868
H	1.175425	-11.047107	0.087866
H	0.475528	10.922234	0.517558
H	0.161539	10.792087	-1.208158
H	-0.161540	-10.792088	1.208156
H	-0.475528	-10.922234	-0.517560
C	-2.827395	-0.422136	-0.130809
H	-3.124331	-0.962277	-1.031747
H	-3.202841	-0.982970	0.727152
H	-3.297236	0.557433	-0.140527
C	2.827394	0.422136	0.130807
H	3.202840	0.982970	-0.727154
H	3.124331	0.962277	1.031745
H	3.297236	-0.557434	0.140526

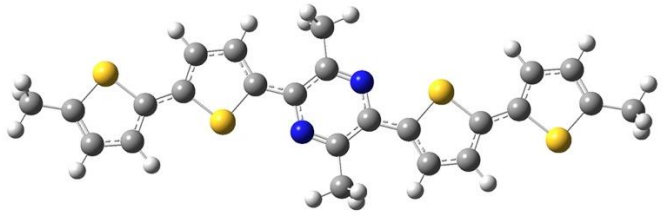


Figure S20. Optimized S_1 geometry of MePyrz(TT)$_2$ with C_{2h} symmetry.

Table S8. Cartesian coordinates (in Å) of the B3LYP/6-311G(2*df*, 2*pd*) optimized S_1 geometry of MePyrz(TT)$_2$ with C_{2h} symmetry.

C	-1.449700	6.932479	0.000000
C	-0.126866	6.515529	0.000000
S	0.928351	7.922284	0.000000
C	-0.415338	9.022962	0.000000
C	-1.600213	8.330499	0.000000
C	0.394295	5.195188	0.000000
S	-0.656206	3.796259	0.000000
C	0.716958	2.692591	0.000000
C	1.915041	3.421502	0.000000
C	1.733146	4.796938	0.000000
C	0.414345	1.301664	0.000000
C	1.348882	0.222352	0.000000
N	0.924565	-1.019790	0.000000
C	-0.414345	-1.301664	0.000000
C	-1.348882	-0.222352	0.000000
N	-0.924565	1.019790	0.000000
C	-0.716958	-2.692591	0.000000
S	0.656206	-3.796259	0.000000
C	-0.394295	-5.195188	0.000000
C	-1.733146	-4.796938	0.000000
C	-1.915041	-3.421502	0.000000
C	0.126866	-6.515529	0.000000
C	1.449700	-6.932479	0.000000
C	1.600213	-8.330499	0.000000
C	0.415338	-9.022962	0.000000
S	-0.928351	-7.922284	0.000000
C	0.208784	-10.500324	0.000000
C	-0.208784	10.500324	0.000000
H	2.551288	5.502925	0.000000
H	-2.551288	-5.502925	0.000000

H	-2.277549	6.238965	0.000000
H	2.277549	-6.238965	0.000000
H	-2.559603	8.828617	0.000000
H	2.559603	-8.828617	0.000000
H	2.888845	2.965342	0.000000
H	-2.888845	-2.965342	0.000000
H	-1.171845	11.009289	0.000000
H	1.171845	-11.009289	0.000000
H	0.347756	10.834945	0.878875
H	0.347756	10.834945	-0.878875
H	-0.347756	-10.834945	0.878875
H	-0.347756	-10.834945	-0.878875
C	-2.839669	-0.407099	0.000000
H	-3.174473	-0.958348	-0.880677
H	-3.174473	-0.958348	0.880677
H	-3.310701	0.571990	0.000000
C	2.839669	0.407099	0.000000
H	3.174473	0.958348	-0.880677
H	3.174473	0.958348	0.880677
H	3.310701	-0.571990	0.000000

Spectroscopic Analysis

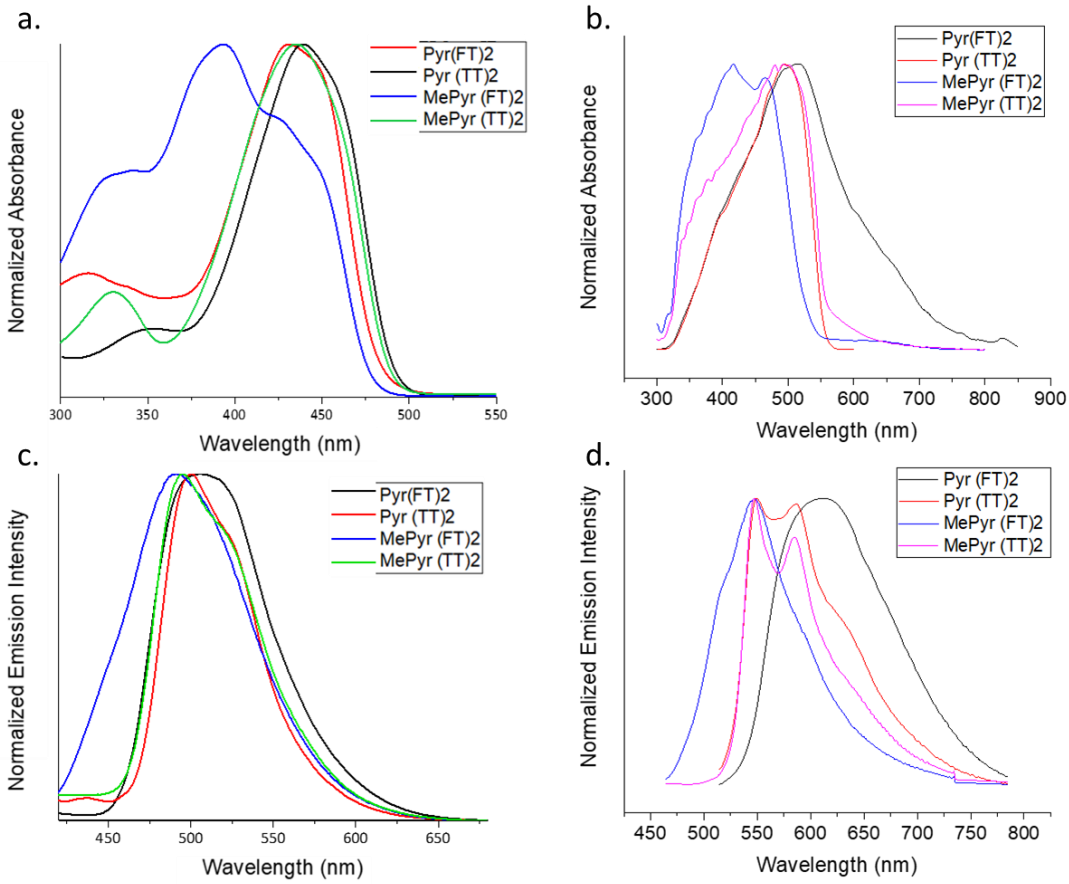


Figure S21. Solution-state absorption/fluorescence spectra in DCM (a, c); solid-state diffuse reflectance and emission spectra (b,d)

Excited-State Lifetimes

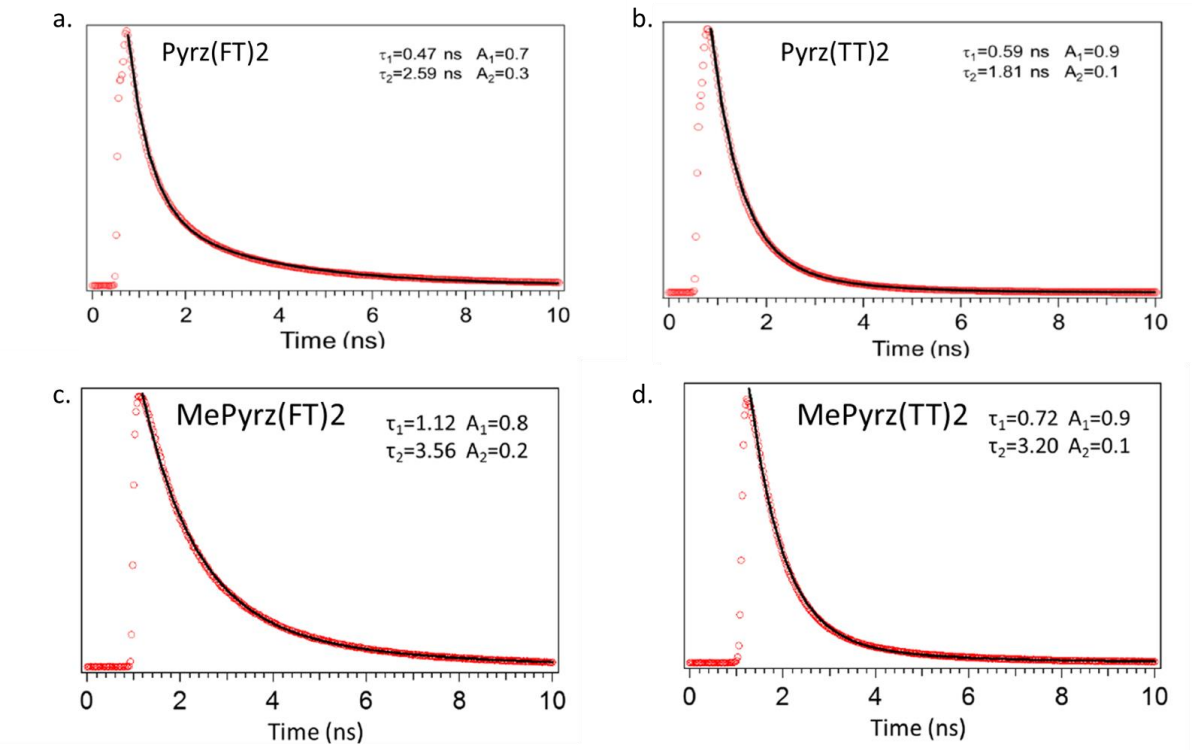


Figure S22. Excited state lifetime in the solid-state

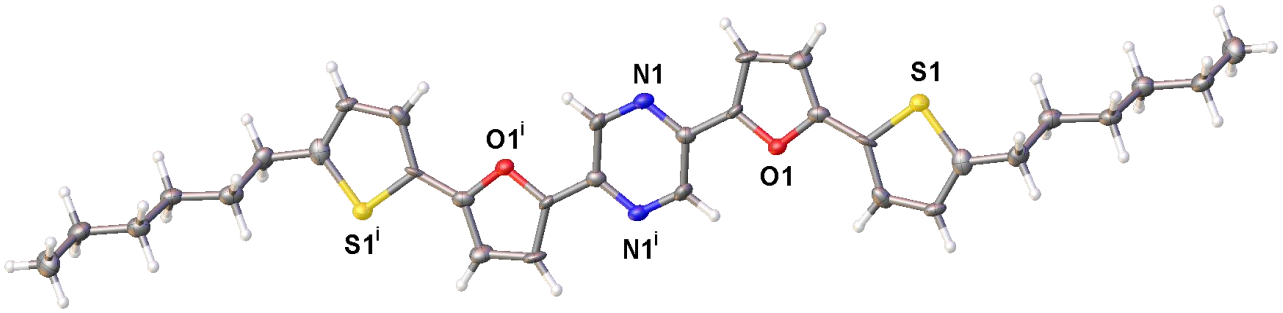


Table S1. Crystal data and structure refinement for Pyrz(FT)$_2$

Identification code	DK121117/LNP23	
Empirical formula	C32 H36 N2 O2 S2	
Formula weight	544.75	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.4937(15) Å	α= 90°.
	b = 4.7436(4) Å	β= 106.926(5)°.
	c = 18.9806(18) Å	γ = 90°.
Volume	1420.7(2) Å^3	
Z	2	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	1.942 mm^{-1}	
F(000)	580	
Crystal size	0.22 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.800 to 68.351°.	
Index ranges	-19<=h<=19, -5<=k<=5, -22<=l<=22	
Reflections collected	8176	
Independent reflections	2596 [R(int) = 0.0617]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5928	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2596 / 0 / 173	
Goodness-of-fit on F^2	0.969	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1224	
R indices (all data)	R1 = 0.0780, wR2 = 0.1354	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.423 and -0.273 e.Å^{-3}	

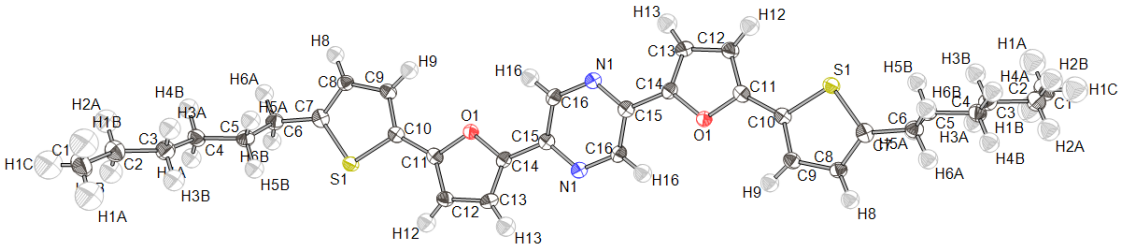


Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Pyrz(FT)$_2$ U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2433(1)	11090(2)	2674(1)	26(1)
O(1)	983(1)	5327(4)	1370(1)	24(1)
N(1)	701(2)	835(5)	-220(1)	27(1)
C(12)	2228(2)	6892(6)	1282(2)	29(1)
C(9)	998(2)	8957(6)	2639(2)	26(1)
C(6)	2411(2)	14183(6)	3924(2)	29(1)
C(8)	1201(2)	10883(6)	3235(2)	26(1)
C(3)	4367(2)	13265(7)	5661(2)	34(1)
C(7)	1962(2)	12223(6)	3337(2)	27(1)
C(5)	3212(2)	12882(7)	4449(2)	30(1)
C(13)	1915(2)	4862(7)	730(2)	31(1)
C(2)	4817(2)	15090(8)	6315(2)	42(1)
C(1)	5556(2)	13597(9)	6858(2)	48(1)
C(15)	550(2)	1910(6)	383(2)	23(1)
C(14)	1159(2)	3964(6)	795(2)	24(1)
C(10)	1608(2)	8821(5)	2278(2)	23(1)
C(11)	1646(2)	7138(6)	1666(2)	24(1)
C(16)	154(2)	-1059(6)	-596(2)	27(1)
C(4)	3637(2)	14734(6)	5106(2)	31(1)

Table S3. Bond lengths [Å] and angles [°] for Pyrz(FT)$_2$

S(1)-C(7)	1.744(3)
S(1)-C(10)	1.726(3)
O(1)-C(14)	1.370(3)
O(1)-C(11)	1.374(3)
N(1)-C(15)	1.342(4)
N(1)-C(16)	1.326(4)
C(12)-H(12)	0.9500
C(12)-C(13)	1.406(4)
C(12)-C(11)	1.369(4)
C(9)-H(9)	0.9500
C(9)-C(8)	1.416(4)
C(9)-C(10)	1.374(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(7)	1.475(4)
C(6)-C(5)	1.534(4)
C(8)-H(8)	0.9500
C(8)-C(7)	1.369(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(2)	1.518(5)
C(3)-C(4)	1.519(4)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(4)	1.519(4)
C(13)-H(13)	0.9500
C(13)-C(14)	1.357(4)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(1)	1.522(5)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(15)-C(14)	1.453(4)
C(15)-C(16)#1	1.395(4)
C(10)-C(11)	1.425(4)
C(16)-H(16)	0.9500

C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900

C(10)-S(1)-C(7)	92.68(14)
C(14)-O(1)-C(11)	107.1(2)
C(16)-N(1)-C(15)	116.8(2)
C(13)-C(12)-H(12)	126.5
C(11)-C(12)-H(12)	126.5
C(11)-C(12)-C(13)	107.1(3)
C(8)-C(9)-H(9)	123.5
C(10)-C(9)-H(9)	123.5
C(10)-C(9)-C(8)	113.1(2)
H(6A)-C(6)-H(6B)	107.8
C(7)-C(6)-H(6A)	109.1
C(7)-C(6)-H(6B)	109.1
C(7)-C(6)-C(5)	112.7(2)
C(5)-C(6)-H(6A)	109.1
C(5)-C(6)-H(6B)	109.1
C(9)-C(8)-H(8)	123.0
C(7)-C(8)-C(9)	113.9(3)
C(7)-C(8)-H(8)	123.0
H(3A)-C(3)-H(3B)	107.7
C(2)-C(3)-H(3A)	108.8
C(2)-C(3)-H(3B)	108.8
C(2)-C(3)-C(4)	113.9(3)
C(4)-C(3)-H(3A)	108.8
C(4)-C(3)-H(3B)	108.8
C(6)-C(7)-S(1)	120.6(2)
C(8)-C(7)-S(1)	109.7(2)
C(8)-C(7)-C(6)	129.6(3)
C(6)-C(5)-H(5A)	108.8
C(6)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7
C(4)-C(5)-C(6)	113.9(2)
C(4)-C(5)-H(5A)	108.8
C(4)-C(5)-H(5B)	108.8
C(12)-C(13)-H(13)	126.5

C(14)-C(13)-C(12)	107.1(3)
C(14)-C(13)-H(13)	126.5
C(3)-C(2)-H(2A)	109.0
C(3)-C(2)-H(2B)	109.0
C(3)-C(2)-C(1)	113.1(3)
H(2A)-C(2)-H(2B)	107.8
C(1)-C(2)-H(2A)	109.0
C(1)-C(2)-H(2B)	109.0
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(15)-C(14)	116.3(2)
N(1)-C(15)-C(16)#1	120.9(3)
C(16)#1-C(15)-C(14)	122.8(3)
O(1)-C(14)-C(15)	118.1(2)
C(13)-C(14)-O(1)	109.8(2)
C(13)-C(14)-C(15)	132.1(3)
C(9)-C(10)-S(1)	110.6(2)
C(9)-C(10)-C(11)	130.1(3)
C(11)-C(10)-S(1)	119.3(2)
O(1)-C(11)-C(10)	117.8(2)
C(12)-C(11)-O(1)	109.0(2)
C(12)-C(11)-C(10)	133.2(3)
N(1)-C(16)-C(15)#1	122.3(3)
N(1)-C(16)-H(16)	118.8
C(15)#1-C(16)-H(16)	118.8
C(3)-C(4)-C(5)	112.8(2)
C(3)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4B)	109.0
C(5)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Pyrz(FT)$_2$ The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	23(1)	27(1)	31(1)	-1(1)	9(1)	-2(1)
O(1)	22(1)	24(1)	24(1)	-1(1)	7(1)	1(1)
N(1)	27(1)	28(1)	26(1)	-1(1)	9(1)	-1(1)
C(12)	29(2)	30(1)	29(2)	1(1)	10(1)	-4(1)
C(9)	23(1)	25(1)	30(2)	2(1)	7(1)	1(1)
C(6)	27(1)	29(1)	32(2)	1(1)	10(1)	2(1)
C(8)	23(1)	28(1)	26(1)	2(1)	7(1)	3(1)
C(3)	32(2)	37(2)	34(2)	1(1)	9(1)	3(1)
C(7)	27(1)	22(1)	30(2)	5(1)	3(1)	6(1)
C(5)	28(2)	30(2)	32(2)	0(1)	11(1)	3(1)
C(13)	33(2)	34(2)	29(2)	0(1)	16(1)	-2(1)
C(2)	30(2)	53(2)	39(2)	-4(2)	4(1)	1(2)
C(1)	38(2)	58(2)	40(2)	7(2)	-1(2)	-3(2)
C(15)	23(1)	21(1)	24(1)	4(1)	5(1)	6(1)
C(14)	26(1)	23(1)	22(1)	0(1)	7(1)	5(1)
C(10)	23(1)	19(1)	27(1)	5(1)	5(1)	2(1)
C(11)	22(1)	23(1)	25(1)	6(1)	2(1)	2(1)
C(16)	29(1)	27(1)	25(1)	-3(1)	9(1)	3(1)
C(4)	25(1)	33(2)	36(2)	-3(1)	7(1)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Pyrz(FT)$_2$

	x	y	z	U(eq)
H(12)	2745	7901	1372	35
H(9)	493	7871	2503	31
H(6A)	2023	14758	4211	35
H(6B)	2569	15898	3698	35
H(8)	842	11215	3537	31
H(3A)	4148	11557	5843	41
H(3B)	4784	12647	5408	41
H(5A)	3062	11058	4631	35
H(5B)	3622	12494	4170	35
H(13)	2182	4238	377	37
H(2A)	4405	15678	6575	50
H(2B)	5030	16813	6133	50
H(1A)	5974	13046	6607	72
H(1B)	5349	11912	7049	72
H(1C)	5821	14871	7266	72
H(16)	243	-1865	-1025	32
H(4A)	3852	16464	4929	38
H(4B)	3211	15308	5353	38

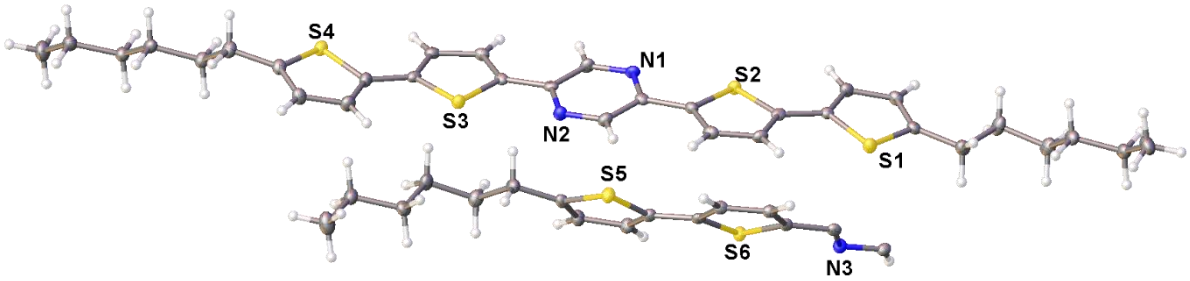


Table S6. Crystal data and structure refinement for Pyrz(TT)$_2$

Identification code	pyrzTh2 (DK052518)	
Empirical formula	C32 H36 N2 S4	
Formula weight	576.87	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 26.416(3) Å	α= 90°.
	b = 5.6442(5) Å	β= 103.328(3)°.
	c = 29.724(3) Å	γ= 90°.
Volume	4312.5(7) Å^3	
Z, Z'	6, 1.5	
Density (calculated)	1.333 Mg/m^3	
Absorption coefficient	0.356 mm^{-1}	
F(000)	1836	
Crystal size	0.27 x 0.16 x 0.1 mm^3	
Theta range for data collection	1.408 to 25.337°.	
Index ranges	-31<=h<=31, -6<=k<=6, -35<=l<=34	
Reflections collected	26925	
Independent reflections	7833 [R(int) = 0.0516]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6749	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7833 / 0 / 517	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1018	
R indices (all data)	R1 = 0.0754, wR2 = 0.1096	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.375 and -0.447 e.Å^{-3}	

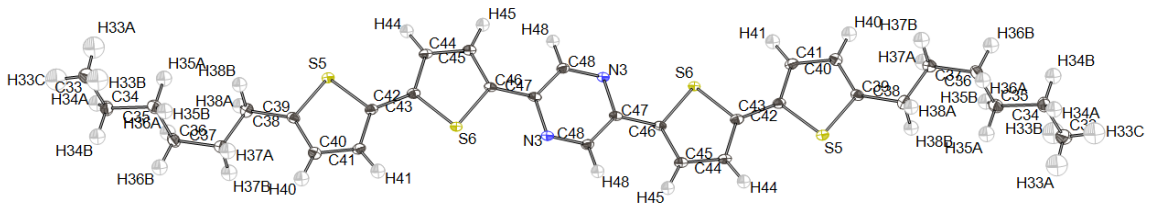


Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Pyrz(TT)$_2$ U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(2)	8118(1)	4712(1)	3348(1)	15(1)
S(3)	5135(1)	6289(1)	3298(1)	16(1)
S(4)	3550(1)	3645(1)	2770(1)	17(1)
S(5)	6970(1)	2960(1)	4395(1)	17(1)
S(1)	9687(1)	7463(1)	3914(1)	17(1)
S(6)	8495(1)	-286(1)	4941(1)	15(1)
N(2)	6262(1)	7028(4)	3443(1)	16(1)
N(1)	6982(1)	4066(4)	3158(1)	16(1)
N(3)	9615(1)	-1312(4)	5144(1)	15(1)
C(19)	5568(1)	4295(5)	3151(1)	14(1)
C(47)	9507(1)	776(5)	4920(1)	14(1)
C(18)	6117(1)	4933(5)	3230(1)	14(1)
C(15)	7127(1)	6159(5)	3371(1)	14(1)
C(39)	6489(1)	1042(5)	4485(1)	16(1)
C(7)	10144(1)	5422(5)	3821(1)	16(1)
C(16)	6759(1)	7601(5)	3512(1)	16(1)
C(14)	7678(1)	6770(5)	3467(1)	13(1)
C(30)	1418(1)	1323(5)	2792(1)	19(1)
C(44)	8210(1)	3708(5)	4556(1)	15(1)
C(21)	4777(1)	2370(5)	2913(1)	16(1)
C(46)	8970(1)	1579(5)	4821(1)	13(1)
C(17)	6482(1)	3513(5)	3089(1)	17(1)

C(45)	8754(1)	3644(5)	4623(1)	15(1)
C(48)	10104(1)	-2044(5)	5222(1)	14(1)
C(41)	7260(1)	-910(5)	4818(1)	18(1)
C(27)	2546(1)	5596(5)	2679(1)	20(1)
C(40)	6709(1)	-915(5)	4717(1)	19(1)
C(28)	2285(1)	3409(5)	2830(1)	18(1)
C(26)	3120(1)	5794(5)	2871(1)	17(1)
C(43)	8007(1)	1709(5)	4708(1)	14(1)
C(8)	9902(1)	3545(5)	3575(1)	17(1)
C(20)	5319(1)	2290(5)	2954(1)	15(1)
C(24)	3932(1)	7320(5)	3226(1)	20(1)
C(42)	7465(1)	1081(5)	4670(1)	15(1)
C(9)	9350(1)	3719(5)	3460(1)	17(1)
C(5)	11069(1)	4056(5)	3885(1)	24(1)
C(38)	5925(1)	1626(5)	4294(1)	19(1)
C(37)	5557(1)	-86(5)	4446(1)	21(1)
C(10)	9170(1)	5745(5)	3619(1)	13(1)
C(12)	8470(1)	8637(5)	3732(1)	16(1)
C(6)	10710(1)	5847(5)	4030(1)	20(1)
C(35)	4771(1)	2671(5)	4425(1)	21(1)
C(11)	8641(1)	6547(5)	3584(1)	14(1)
C(29)	1694(1)	3496(5)	2665(1)	18(1)
C(2)	12464(1)	6843(5)	4124(1)	21(1)
C(22)	4612(1)	4428(5)	3079(1)	14(1)
C(25)	3386(1)	7609(5)	3120(1)	20(1)
C(36)	4983(1)	454(5)	4241(1)	21(1)
C(13)	7926(1)	8767(5)	3665(1)	17(1)
C(23)	4090(1)	5263(5)	3060(1)	16(1)
C(4)	11646(1)	4461(5)	4107(1)	23(1)
C(34)	4178(1)	2821(6)	4276(1)	22(1)
C(32)	558(1)	-723(6)	2776(1)	31(1)
C(3)	11874(1)	6734(5)	3962(1)	21(1)
C(31)	825(1)	1475(5)	2650(1)	21(1)
C(33)	3955(1)	4992(6)	4466(1)	32(1)
C(1)	12695(1)	9168(6)	4010(1)	29(1)

Table S8. Bond lengths [Å] and angles [°] for Pyrz(TT)$_2$

S(2)-C(14)	1.737(3)
S(2)-C(11)	1.739(3)
S(3)-C(19)	1.730(3)
S(3)-C(22)	1.738(3)
S(4)-C(26)	1.733(3)
S(4)-C(23)	1.745(3)
S(5)-C(39)	1.736(3)
S(5)-C(42)	1.735(3)
S(1)-C(7)	1.736(3)
S(1)-C(10)	1.738(3)
S(6)-C(46)	1.737(3)
S(6)-C(43)	1.730(3)
N(2)-C(18)	1.355(3)
N(2)-C(16)	1.321(4)
N(1)-C(15)	1.353(4)
N(1)-C(17)	1.327(4)
N(3)-C(47)	1.351(3)
N(3)-C(48)	1.325(4)
C(19)-C(18)	1.461(4)
C(19)-C(20)	1.369(4)
C(47)-C(46)	1.454(4)
C(47)-C(48)#1	1.396(4)
C(18)-C(17)	1.392(4)
C(15)-C(16)	1.405(4)
C(15)-C(14)	1.457(4)
C(39)-C(40)	1.360(4)
C(39)-C(38)	1.503(4)
C(7)-C(8)	1.359(4)
C(7)-C(6)	1.503(4)
C(14)-C(13)	1.368(4)
C(30)-C(29)	1.519(4)
C(30)-C(31)	1.527(4)
C(44)-C(45)	1.407(4)
C(44)-C(43)	1.369(4)
C(21)-C(20)	1.409(4)

C(21)-C(22)	1.372(4)
C(46)-C(45)	1.369(4)
C(48)-C(47)#1	1.396(4)
C(41)-C(40)	1.417(4)
C(41)-C(42)	1.364(4)
C(27)-C(28)	1.531(4)
C(27)-C(26)	1.498(4)
C(28)-C(29)	1.525(4)
C(26)-C(25)	1.360(4)
C(43)-C(42)	1.455(4)
C(8)-C(9)	1.423(4)
C(24)-C(25)	1.412(4)
C(24)-C(23)	1.364(4)
C(9)-C(10)	1.364(4)
C(5)-C(6)	1.514(4)
C(5)-C(4)	1.533(4)
C(38)-C(37)	1.511(4)
C(37)-C(36)	1.528(4)
C(10)-C(11)	1.449(4)
C(12)-C(11)	1.372(4)
C(12)-C(13)	1.409(4)
C(35)-C(36)	1.524(4)
C(35)-C(34)	1.530(4)
C(2)-C(3)	1.523(4)
C(2)-C(1)	1.517(4)
C(22)-C(23)	1.446(4)
C(4)-C(3)	1.520(4)
C(34)-C(33)	1.521(4)
C(32)-C(31)	1.517(4)

C(14)-S(2)-C(11)	91.58(14)
C(19)-S(3)-C(22)	91.56(14)
C(26)-S(4)-C(23)	92.37(14)
C(42)-S(5)-C(39)	92.61(14)
C(7)-S(1)-C(10)	92.48(14)
C(43)-S(6)-C(46)	91.67(14)
C(16)-N(2)-C(18)	116.7(2)

C(17)-N(1)-C(15)	116.3(2)
C(48)-N(3)-C(47)	116.4(2)
C(18)-C(19)-S(3)	119.2(2)
C(20)-C(19)-S(3)	111.4(2)
C(20)-C(19)-C(18)	129.3(3)
N(3)-C(47)-C(46)	117.3(2)
N(3)-C(47)-C(48)#1	120.6(3)
C(48)#1-C(47)-C(46)	122.1(3)
N(2)-C(18)-C(19)	117.0(2)
N(2)-C(18)-C(17)	120.2(3)
C(17)-C(18)-C(19)	122.8(3)
N(1)-C(15)-C(16)	120.3(3)
N(1)-C(15)-C(14)	117.3(2)
C(16)-C(15)-C(14)	122.2(3)
C(40)-C(39)-S(5)	110.0(2)
C(40)-C(39)-C(38)	129.9(3)
C(38)-C(39)-S(5)	120.1(2)
C(8)-C(7)-S(1)	110.2(2)
C(8)-C(7)-C(6)	130.3(3)
C(6)-C(7)-S(1)	119.4(2)
N(2)-C(16)-C(15)	122.9(3)
C(15)-C(14)-S(2)	119.2(2)
C(13)-C(14)-S(2)	111.2(2)
C(13)-C(14)-C(15)	129.5(3)
C(29)-C(30)-C(31)	114.0(2)
C(43)-C(44)-C(45)	113.4(3)
C(22)-C(21)-C(20)	113.4(3)
C(47)-C(46)-S(6)	119.1(2)
C(45)-C(46)-S(6)	110.9(2)
C(45)-C(46)-C(47)	130.0(3)
N(1)-C(17)-C(18)	123.5(3)
C(46)-C(45)-C(44)	113.1(3)
N(3)-C(48)-C(47)#1	123.0(3)
C(42)-C(41)-C(40)	113.4(3)
C(26)-C(27)-C(28)	115.7(2)
C(39)-C(40)-C(41)	113.9(3)
C(29)-C(28)-C(27)	112.1(2)

C(27)-C(26)-S(4)	121.9(2)
C(25)-C(26)-S(4)	110.2(2)
C(25)-C(26)-C(27)	127.9(3)
C(44)-C(43)-S(6)	110.9(2)
C(44)-C(43)-C(42)	128.8(3)
C(42)-C(43)-S(6)	120.1(2)
C(7)-C(8)-C(9)	113.8(3)
C(19)-C(20)-C(21)	112.9(3)
C(23)-C(24)-C(25)	113.6(3)
C(41)-C(42)-S(5)	110.1(2)
C(41)-C(42)-C(43)	129.2(3)
C(43)-C(42)-S(5)	120.7(2)
C(10)-C(9)-C(8)	113.2(3)
C(6)-C(5)-C(4)	113.8(3)
C(39)-C(38)-C(37)	113.4(2)
C(38)-C(37)-C(36)	113.7(2)
C(9)-C(10)-S(1)	110.3(2)
C(9)-C(10)-C(11)	130.1(3)
C(11)-C(10)-S(1)	119.6(2)
C(11)-C(12)-C(13)	113.6(3)
C(7)-C(6)-C(5)	113.8(2)
C(36)-C(35)-C(34)	112.3(3)
C(10)-C(11)-S(2)	120.4(2)
C(12)-C(11)-S(2)	110.6(2)
C(12)-C(11)-C(10)	128.9(3)
C(30)-C(29)-C(28)	114.1(2)
C(1)-C(2)-C(3)	113.6(3)
C(21)-C(22)-S(3)	110.7(2)
C(21)-C(22)-C(23)	129.9(3)
C(23)-C(22)-S(3)	119.1(2)
C(26)-C(25)-C(24)	114.0(3)
C(35)-C(36)-C(37)	115.7(3)
C(14)-C(13)-C(12)	112.9(3)
C(24)-C(23)-S(4)	109.9(2)
C(24)-C(23)-C(22)	129.2(3)
C(22)-C(23)-S(4)	120.8(2)
C(3)-C(4)-C(5)	115.1(3)

C(33)-C(34)-C(35)	113.3(3)
C(4)-C(3)-C(2)	112.8(2)
C(32)-C(31)-C(30)	113.1(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Pyrz(TT)$_2$ The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(2)	17(1)	9(1)	19(1)	-2(1)	4(1)	0(1)
S(3)	16(1)	11(1)	19(1)	-3(1)	3(1)	0(1)
S(4)	16(1)	12(1)	21(1)	0(1)	2(1)	-1(1)
S(5)	16(1)	12(1)	21(1)	3(1)	3(1)	0(1)
S(1)	18(1)	12(1)	21(1)	-2(1)	4(1)	-1(1)
S(6)	15(1)	10(1)	20(1)	3(1)	4(1)	-1(1)
N(2)	17(1)	11(1)	18(1)	-2(1)	3(1)	1(1)
N(1)	20(1)	12(1)	15(1)	-4(1)	2(1)	2(1)
N(3)	16(1)	10(1)	18(1)	2(1)	4(1)	-1(1)
C(19)	18(2)	11(1)	12(1)	4(1)	4(1)	4(1)
C(47)	19(2)	8(1)	14(2)	-2(1)	4(1)	-2(1)
C(18)	20(2)	11(1)	9(1)	2(1)	2(1)	3(1)
C(15)	19(2)	11(1)	12(2)	4(1)	5(1)	2(1)
C(39)	17(2)	13(1)	19(2)	-3(1)	7(1)	-3(1)
C(7)	19(2)	15(2)	15(2)	1(1)	7(1)	1(1)
C(16)	18(2)	11(1)	16(2)	0(1)	0(1)	-1(1)
C(14)	16(2)	11(1)	13(2)	1(1)	4(1)	3(1)
C(30)	18(2)	19(2)	19(2)	1(1)	4(1)	0(1)
C(44)	20(2)	9(1)	16(2)	1(1)	4(1)	-1(1)
C(21)	21(2)	14(2)	13(2)	0(1)	4(1)	-1(1)
C(46)	16(2)	9(1)	15(2)	-2(1)	4(1)	-2(1)
C(17)	19(2)	10(1)	19(2)	-4(1)	2(1)	-1(1)
C(45)	20(2)	10(1)	15(2)	0(1)	4(1)	-1(1)
C(48)	17(2)	11(1)	14(2)	2(1)	1(1)	-1(1)
C(41)	19(2)	13(2)	20(2)	3(1)	3(1)	3(1)

C(27)	18(2)	16(2)	25(2)	4(1)	2(1)	1(1)
C(40)	18(2)	17(2)	24(2)	3(1)	6(1)	-1(1)
C(28)	18(2)	14(2)	22(2)	2(1)	3(1)	-1(1)
C(26)	18(2)	13(2)	21(2)	4(1)	4(1)	0(1)
C(43)	19(2)	10(1)	11(1)	-3(1)	2(1)	1(1)
C(8)	21(2)	12(1)	20(2)	0(1)	8(1)	2(1)
C(20)	21(2)	10(1)	15(2)	1(1)	5(1)	2(1)
C(24)	20(2)	16(2)	22(2)	-3(1)	3(1)	-4(1)
C(42)	18(2)	10(1)	16(2)	-1(1)	2(1)	1(1)
C(9)	19(2)	14(2)	18(2)	-2(1)	6(1)	-3(1)
C(5)	17(2)	16(2)	35(2)	-4(1)	0(1)	3(1)
C(38)	17(2)	20(2)	18(2)	1(1)	3(1)	2(1)
C(37)	21(2)	16(2)	27(2)	2(1)	3(1)	-1(1)
C(10)	16(2)	10(1)	12(2)	2(1)	4(1)	-1(1)
C(12)	21(2)	11(1)	16(2)	-1(1)	1(1)	-3(1)
C(6)	20(2)	18(2)	23(2)	-3(1)	7(1)	-2(1)
C(35)	21(2)	22(2)	21(2)	1(1)	8(1)	-3(1)
C(11)	20(2)	10(1)	13(2)	4(1)	3(1)	-2(1)
C(29)	17(2)	17(2)	18(2)	-3(1)	2(1)	2(1)
C(2)	19(2)	24(2)	21(2)	-2(1)	5(1)	4(1)
C(22)	18(2)	11(1)	11(1)	1(1)	1(1)	-2(1)
C(25)	20(2)	14(2)	26(2)	-1(1)	8(1)	0(1)
C(36)	17(2)	20(2)	25(2)	-3(1)	4(1)	-4(1)
C(13)	22(2)	11(1)	16(2)	0(1)	5(1)	4(1)
C(23)	15(2)	15(2)	18(2)	2(1)	3(1)	-1(1)
C(4)	21(2)	18(2)	30(2)	-1(1)	1(1)	4(1)
C(34)	17(2)	25(2)	23(2)	4(1)	4(1)	-1(1)
C(32)	22(2)	34(2)	38(2)	1(2)	10(2)	-4(2)
C(3)	19(2)	23(2)	21(2)	3(1)	4(1)	6(1)
C(31)	19(2)	24(2)	21(2)	-1(1)	5(1)	-1(1)
C(33)	26(2)	25(2)	48(2)	2(2)	14(2)	-1(2)
C(1)	24(2)	35(2)	31(2)	7(2)	14(2)	6(2)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Pyrz(TT)$_2$

	x	y	z	U(eq)
H(16)	6872	9053	3664	19
H(30A)	1525	1087	3131	22
H(30B)	1532	-82	2642	22
H(44)	8002	5011	4420	18
H(21)	4549	1121	2784	19
H(17)	6367	2070	2934	20
H(45)	8952	4904	4539	18
H(48)	10193	-3499	5381	17
H(41)	7467	-2170	4975	21
H(27A)	2479	5592	2337	24
H(27B)	2377	7026	2770	24
H(40)	6512	-2171	4803	23
H(28A)	2417	1970	2705	22
H(28B)	2379	3300	3172	22
H(8)	10085	2237	3488	20
H(20)	5493	984	2856	18
H(24)	4166	8450	3396	23
H(9)	9129	2543	3289	20
H(5A)	11018	4114	3545	28
H(5B)	10970	2450	3968	28
H(38A)	5854	1627	3952	22
H(38B)	5856	3243	4394	22
H(37A)	5621	-48	4787	26
H(37B)	5634	-1709	4354	26
H(12)	8698	9879	3867	20
H(6A)	10767	5811	4371	24
H(6B)	10805	7450	3942	24
H(35A)	4924	4088	4311	25
H(35B)	4879	2673	4767	25

H(29A)	1564	4914	2799	21
H(29B)	1604	3677	2324	21
H(2A)	12562	6596	4462	26
H(2B)	12617	5533	3977	26
H(25)	3219	8951	3214	23
H(36A)	4932	615	3902	25
H(36B)	4775	-921	4299	25
H(13)	7749	10102	3750	20
H(4A)	11692	4477	4447	28
H(4B)	11847	3104	4029	28
H(34A)	4072	2850	3935	26
H(34B)	4026	1381	4384	26
H(32A)	656	-2095	2613	46
H(32B)	180	-505	2687	46
H(32C)	665	-988	3111	46
H(3A)	11721	8104	4091	25
H(3B)	11776	6864	3621	25
H(31A)	709	2867	2803	26
H(31B)	717	1724	2312	26
H(33A)	4078	6427	4338	48
H(33B)	4070	5012	4803	48
H(33C)	3575	4935	4376	48
H(1A)	12585	9469	3677	43
H(1B)	13075	9078	4101	43
H(1C)	12574	10458	4180	43

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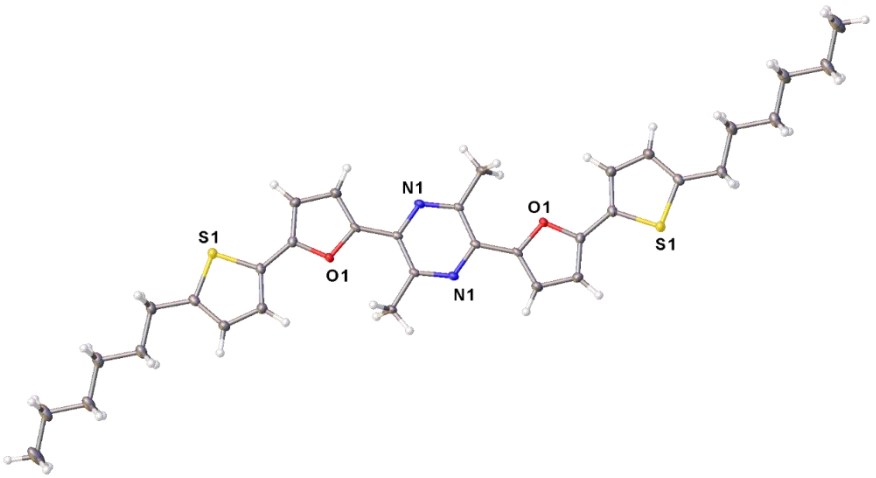

Table S11. Crystal data and structure refinement for MePyrz(FT)$_2$

Identification code	TFMePtr2FT	
Empirical formula	C34 H40 N2 O2 S2	
Formula weight	572.80	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.1067(9) Å	α= 80.476(4)°.
	b = 7.1680(8) Å	β= 86.864(6)°.
	c = 20.766(3) Å	γ = 86.423(5)°.
Volume	747.43(19) Å^3	
Z	1	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.212 mm^{-1}	
F(000)	306	
Crystal size	0.33 x 0.29 x 0.24 mm^3	
Theta range for data collection	1.991 to 26.394°.	
Index ranges	-6<=h<=6, -8<=k<=8, -25<=l<=22	
Reflections collected	6950	
Independent reflections	3063 [R(int) = 0.0297]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.7077	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3063 / 0 / 183	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0876	
R indices (all data)	R1 = 0.0479, wR2 = 0.0920	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.369 and -0.210 e.Å^{-3}	

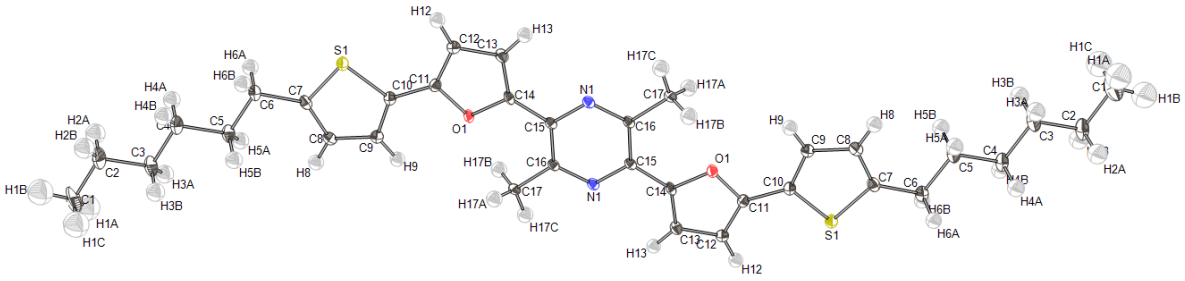

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for MePyrz(FT)$_2$ U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5385(1)	-551(1)	7560(1)	17(1)
O(1)	124(2)	287(2)	6173(1)	14(1)
N(1)	-4532(3)	-1843(2)	5311(1)	13(1)
C(15)	-3199(3)	-418(2)	5459(1)	12(1)
C(10)	3385(3)	463(2)	6934(1)	14(1)
C(14)	-1310(3)	-1036(2)	5962(1)	13(1)
C(12)	1323(3)	-2566(2)	6723(1)	16(1)
C(11)	1721(3)	-679(2)	6640(1)	14(1)
C(17)	-7746(3)	-3131(2)	4726(1)	16(1)
C(9)	3615(3)	2382(2)	6800(1)	17(1)
C(16)	-6331(3)	-1468(2)	4859(1)	12(1)
C(8)	5396(3)	3023(2)	7206(1)	18(1)
C(7)	6500(3)	1626(2)	7648(1)	16(1)
C(13)	-630(3)	-2793(2)	6287(1)	16(1)
C(6)	8404(3)	1760(2)	8164(1)	19(1)
C(4)	10668(4)	3966(3)	8771(1)	22(1)
C(3)	10979(4)	6014(3)	8856(1)	26(1)

C(5)	8815(3)	3803(2)	8236(1)	21(1)
C(1)	13084(5)	8231(3)	9489(1)	40(1)
C(2)	12859(4)	6196(3)	9382(1)	30(1)

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Table S13. Bond lengths [Å] and angles [°] for MePyrz(FT)$_2$

S(1)-C(10)	1.7325(16)
S(1)-C(7)	1.7353(16)
O(1)-C(14)	1.3741(18)
O(1)-C(11)	1.3702(19)
N(1)-C(15)	1.3478(19)
N(1)-C(16)	1.332(2)
C(15)-C(14)	1.456(2)
C(15)-C(16)#1	1.415(2)
C(10)-C(11)	1.441(2)
C(10)-C(9)	1.369(2)
C(14)-C(13)	1.360(2)
C(12)-H(12)	0.9500
C(12)-C(11)	1.361(2)
C(12)-C(13)	1.417(2)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(17)-C(16)	1.503(2)
C(9)-H(9)	0.9500
C(9)-C(8)	1.420(2)
C(8)-H(8)	0.9500
C(8)-C(7)	1.359(2)
C(7)-C(6)	1.503(2)
C(13)-H(13)	0.9500
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(5)	1.525(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(3)	1.526(2)
C(4)-C(5)	1.521(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(2)	1.521(2)
C(5)-H(5A)	0.9900

C(5)-H(5B)	0.9900
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(1)-C(2)	1.523(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900

C(10)-S(1)-C(7)	92.35(8)
C(11)-O(1)-C(14)	106.76(12)
C(16)-N(1)-C(15)	119.43(13)
N(1)-C(15)-C(14)	113.32(13)
N(1)-C(15)-C(16)#1	121.06(14)
C(16)#1-C(15)-C(14)	125.62(14)
C(11)-C(10)-S(1)	120.80(12)
C(9)-C(10)-S(1)	110.73(12)
C(9)-C(10)-C(11)	128.44(15)
O(1)-C(14)-C(15)	119.25(13)
C(13)-C(14)-O(1)	109.71(14)
C(13)-C(14)-C(15)	131.04(14)
C(11)-C(12)-H(12)	126.7
C(11)-C(12)-C(13)	106.62(14)
C(13)-C(12)-H(12)	126.7
O(1)-C(11)-C(10)	115.73(13)
C(12)-C(11)-O(1)	109.99(13)
C(12)-C(11)-C(10)	134.28(15)
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
C(10)-C(9)-H(9)	123.7
C(10)-C(9)-C(8)	112.58(15)
C(8)-C(9)-H(9)	123.7
N(1)-C(16)-C(15)#1	119.51(14)
N(1)-C(16)-C(17)	116.19(14)

C(15)#1-C(16)-C(17)	124.30(14)
C(9)-C(8)-H(8)	122.9
C(7)-C(8)-C(9)	114.16(15)
C(7)-C(8)-H(8)	122.9
C(8)-C(7)-S(1)	110.16(12)
C(8)-C(7)-C(6)	129.42(15)
C(6)-C(7)-S(1)	120.42(12)
C(14)-C(13)-C(12)	106.92(14)
C(14)-C(13)-H(13)	126.5
C(12)-C(13)-H(13)	126.5
C(7)-C(6)-H(6A)	109.1
C(7)-C(6)-H(6B)	109.1
C(7)-C(6)-C(5)	112.54(14)
H(6A)-C(6)-H(6B)	107.8
C(5)-C(6)-H(6A)	109.1
C(5)-C(6)-H(6B)	109.1
H(4A)-C(4)-H(4B)	107.8
C(3)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4B)	109.0
C(5)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
C(5)-C(4)-C(3)	112.73(15)
C(4)-C(3)-H(3A)	108.9
C(4)-C(3)-H(3B)	108.9
H(3A)-C(3)-H(3B)	107.8
C(2)-C(3)-C(4)	113.19(16)
C(2)-C(3)-H(3A)	108.9
C(2)-C(3)-H(3B)	108.9
C(6)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5B)	108.9
C(4)-C(5)-C(6)	113.33(15)
C(4)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5B)	108.9
H(5A)-C(5)-H(5B)	107.7
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5

C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
C(3)-C(2)-C(1)	113.40(18)
C(3)-C(2)-H(2A)	108.9
C(3)-C(2)-H(2B)	108.9
C(1)-C(2)-H(2A)	108.9
C(1)-C(2)-H(2B)	108.9
H(2A)-C(2)-H(2B)	107.7

Symmetry transformations used to generate equivalent atoms:
#1 -x-1,-y,-z+1

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for MePyrz(FT)$_2$ The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	18(1)	16(1)	17(1)	-3(1)	-5(1)	-2(1)
O(1)	15(1)	12(1)	15(1)	-3(1)	-4(1)	-2(1)
N(1)	13(1)	11(1)	15(1)	-4(1)	1(1)	-2(1)
C(15)	12(1)	11(1)	14(1)	-5(1)	2(1)	-2(1)
C(10)	13(1)	18(1)	13(1)	-4(1)	0(1)	-1(1)
C(14)	12(1)	14(1)	16(1)	-8(1)	2(1)	-5(1)
C(12)	17(1)	15(1)	18(1)	-2(1)	-2(1)	0(1)
C(11)	13(1)	17(1)	12(1)	-3(1)	-1(1)	0(1)
C(17)	16(1)	10(1)	23(1)	-4(1)	-4(1)	-3(1)
C(9)	17(1)	16(1)	18(1)	-2(1)	-3(1)	0(1)
C(16)	11(1)	12(1)	15(1)	-5(1)	2(1)	-2(1)
C(8)	19(1)	16(1)	21(1)	-5(1)	-2(1)	-3(1)
C(7)	14(1)	18(1)	17(1)	-8(1)	2(1)	-2(1)
C(13)	18(1)	14(1)	18(1)	-3(1)	-1(1)	-4(1)
C(6)	18(1)	22(1)	18(1)	-6(1)	-4(1)	-2(1)
C(4)	20(1)	30(1)	20(1)	-7(1)	-2(1)	-7(1)
C(3)	28(1)	31(1)	21(1)	-6(1)	-1(1)	-14(1)
C(5)	20(1)	25(1)	20(1)	-4(1)	-2(1)	-7(1)
C(1)	51(1)	46(1)	28(1)	-13(1)	-1(1)	-26(1)

C(2)	27(1)	40(1)	27(1)	-15(1)	-1(1)	-12(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $MePyrz(FT)_2$

	x	y	z	U(eq)
H(12)	2186	-3540	7016	20
H(17A)	-7324	-3332	4275	24
H(17B)	-9644	-2879	4785	24
H(17C)	-7193	-4267	5029	24
H(9)	2685	3195	6470	20
H(8)	5782	4316	7172	22
H(13)	-1331	-3950	6232	19
H(6A)	10114	1140	8050	23
H(6B)	7741	1068	8588	23
H(4A)	12412	3383	8664	27
H(4B)	9992	3249	9190	27
H(3A)	11626	6734	8435	31
H(3B)	9236	6589	8968	31
H(5A)	9528	4481	7816	26
H(5B)	7093	4433	8335	26
H(1A)	13721	8996	9082	60
H(1B)	14321	8254	9832	60
H(1C)	11357	8751	9622	60
H(2A)	14621	5672	9259	36
H(2B)	12255	5428	9798	36

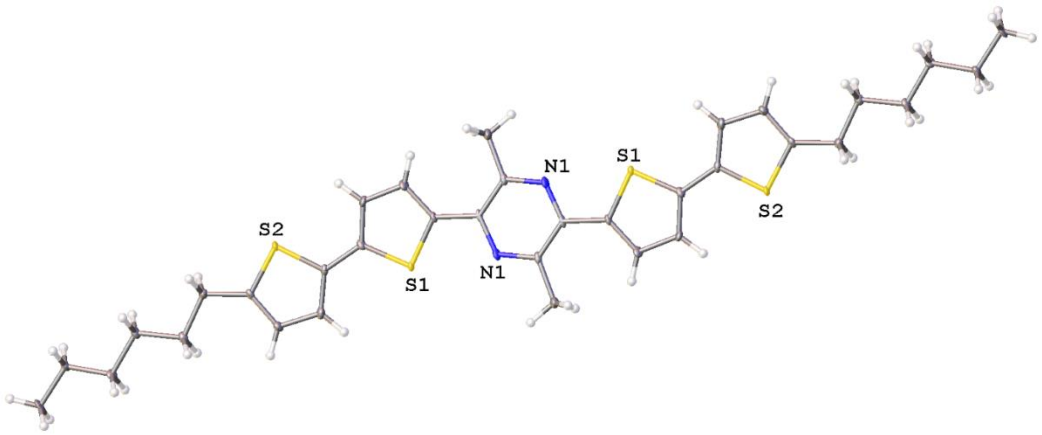

Table S16. Crystal data and structure refinement for MePyrz(TT)$_2$

Report date	2021-02-12	
Identification code	dwat72	
Empirical formula	C34 H40 N2 S4	
Molecular formula	C34 H40 N2 S4	
Formula weight	604.92	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.765(3) Å	α= 80.692(8)°.
	b = 7.688(4) Å	β= 84.686(7)°.
	c = 18.142(9) Å	γ = 71.676(7)°.
Volume	752.4(7) Å^3	
Z	1	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	0.343 mm^{-1}	
F(000)	322	
Crystal size	0.29 x 0.27 x 0.1 mm^3	
Crystal color, habit	yellow plate	
Theta range for data collection	1.139 to 26.518°.	
Index ranges	-7<=h<=7, -9<=k<=9, -22<=l<=22	
Reflections collected	6216	
Independent reflections	3083 [R(int) = 0.0486, R(sigma) = 0.0802]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.677 and 0.511	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3083 / 0 / 184	
Goodness-of-fit on F^2	1.603	
Final R indices [I>2sigma(I)]	R1 = 0.1130, wR2 = 0.3653	
R indices (all data)	R1 = 0.1232, wR2 = 0.3859	
Extinction coefficient	n/a	

Largest diff. peak and hole 1.367 and -0.708 e.Å^{-3}

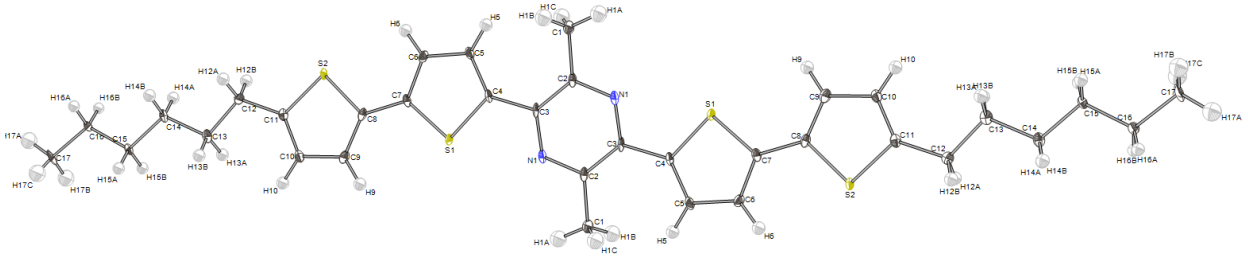

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for MePyrz(TT)$_2$ U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2872(3)	5714(2)	7999(1)	9(1)
S(2)	1868(3)	8163(2)	5650(1)	10(1)
N(1)	1998(12)	4489(8)	9521(3)	10(1)
C(3)	-78(14)	5743(10)	9273(4)	9(2)
C(8)	3193(14)	6955(10)	6476(4)	9(2)
C(13)	7109(14)	7508(10)	3896(4)	11(2)
C(11)	4625(14)	7495(10)	5135(4)	10(2)
C(6)	-740(14)	7873(10)	7255(4)	11(2)
C(16)	8902(13)	8755(10)	1789(4)	10(2)
C(5)	-1705(14)	7598(10)	7996(4)	12(2)
C(10)	6408(14)	6393(10)	5581(4)	11(2)
C(12)	4647(14)	8214(10)	4313(4)	12(2)
C(2)	2128(14)	3733(10)	10239(4)	10(2)
C(15)	9272(13)	7824(10)	2589(4)	10(2)
C(1)	4534(15)	2331(11)	10460(4)	16(2)
C(17)	11194(15)	8296(11)	1284(4)	18(2)
C(14)	6904(14)	8360(10)	3069(4)	12(2)
C(9)	5625(15)	6088(10)	6348(4)	12(2)
C(4)	61(14)	6440(10)	8468(4)	9(2)
C(7)	1719(14)	6962(10)	7163(4)	10(2)

—

Table S18. Bond lengths [Å] and angles [°] for MePyrz(TT)$_2$.

S(1)-C(4)	1.729(7)
S(1)-C(7)	1.725(8)
S(2)-C(8)	1.734(7)
S(2)-C(11)	1.740(7)
N(1)-C(3)	1.341(10)
N(1)-C(2)	1.338(9)
C(3)-C(2)#1	1.401(10)
C(3)-C(4)	1.475(9)
C(8)-C(9)	1.366(11)
C(8)-C(7)	1.442(10)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(13)-C(12)	1.526(10)
C(13)-C(14)	1.536(10)
C(11)-C(10)	1.347(11)
C(11)-C(12)	1.506(10)
C(6)-H(6)	0.9500
C(6)-C(5)	1.417(10)
C(6)-C(7)	1.377(11)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(16)-C(15)	1.513(9)
C(16)-C(17)	1.516(10)
C(5)-H(5)	0.9500
C(5)-C(4)	1.381(11)
C(10)-H(10)	0.9500
C(10)-C(9)	1.428(10)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(2)-C(3)#1	1.401(10)
C(2)-C(1)	1.506(11)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-C(14)	1.528(10)
C(1)-H(1A)	0.9800

C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(9)-H(9)	0.9500

C(7)-S(1)-C(4)	92.2(4)
C(8)-S(2)-C(11)	92.4(4)
C(2)-N(1)-C(3)	120.0(6)
N(1)-C(3)-C(2)#1	120.6(6)
N(1)-C(3)-C(4)	113.6(6)
C(2)#1-C(3)-C(4)	125.9(7)
C(9)-C(8)-S(2)	110.4(5)
C(9)-C(8)-C(7)	129.7(7)
C(7)-C(8)-S(2)	119.9(6)
H(13A)-C(13)-H(13B)	108.2
C(12)-C(13)-H(13A)	109.8
C(12)-C(13)-H(13B)	109.8
C(12)-C(13)-C(14)	109.6(6)
C(14)-C(13)-H(13A)	109.8
C(14)-C(13)-H(13B)	109.8
C(10)-C(11)-S(2)	110.4(5)
C(10)-C(11)-C(12)	131.8(7)
C(12)-C(11)-S(2)	117.8(6)
C(5)-C(6)-H(6)	122.9
C(7)-C(6)-H(6)	122.9
C(7)-C(6)-C(5)	114.1(7)
H(16A)-C(16)-H(16B)	107.6
C(15)-C(16)-H(16A)	108.7
C(15)-C(16)-H(16B)	108.7
C(15)-C(16)-C(17)	114.0(6)
C(17)-C(16)-H(16A)	108.7
C(17)-C(16)-H(16B)	108.7
C(6)-C(5)-H(5)	124.2

C(4)-C(5)-C(6)	111.6(7)
C(4)-C(5)-H(5)	124.2
C(11)-C(10)-H(10)	123.0
C(11)-C(10)-C(9)	114.0(7)
C(9)-C(10)-H(10)	123.0
C(13)-C(12)-H(12A)	108.6
C(13)-C(12)-H(12B)	108.6
C(11)-C(12)-C(13)	114.6(7)
C(11)-C(12)-H(12A)	108.6
C(11)-C(12)-H(12B)	108.6
H(12A)-C(12)-H(12B)	107.6
N(1)-C(2)-C(3)#1	119.4(7)
N(1)-C(2)-C(1)	115.9(6)
C(3)#1-C(2)-C(1)	124.7(6)
C(16)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15B)	109.4
C(16)-C(15)-C(14)	111.4(6)
H(15A)-C(15)-H(15B)	108.0
C(14)-C(15)-H(15A)	109.4
C(14)-C(15)-H(15B)	109.4
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(14)-H(14A)	108.5
C(13)-C(14)-H(14B)	108.5
C(15)-C(14)-C(13)	115.2(7)
C(15)-C(14)-H(14A)	108.5
C(15)-C(14)-H(14B)	108.5

H(14A)-C(14)-H(14B)	107.5
C(8)-C(9)-C(10)	112.9(7)
C(8)-C(9)-H(9)	123.5
C(10)-C(9)-H(9)	123.5
C(3)-C(4)-S(1)	117.2(6)
C(5)-C(4)-S(1)	111.6(5)
C(5)-C(4)-C(3)	131.2(7)
C(8)-C(7)-S(1)	122.7(6)
C(6)-C(7)-S(1)	110.4(5)
C(6)-C(7)-C(8)	126.8(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2

Table S19. Anisotropic displacement parameters ($Å^2$x 10^3) for MePyrz(TT)2. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	11(1)	11(1)	5(1)	0(1)	1(1)	-4(1)
S(2)	11(1)	13(1)	5(1)	0(1)	2(1)	-3(1)
N(1)	13(3)	14(3)	7(3)	-1(2)	2(2)	-9(3)
C(3)	16(4)	9(3)	5(3)	-1(3)	2(3)	-11(3)
C(8)	15(4)	9(3)	6(3)	-1(3)	-1(3)	-6(3)
C(13)	14(4)	12(4)	11(3)	-3(3)	1(3)	-8(3)
C(11)	13(4)	8(3)	9(3)	-4(3)	3(3)	-5(3)
C(6)	13(4)	15(4)	7(3)	1(3)	-3(3)	-6(3)
C(16)	11(4)	10(3)	9(3)	-2(3)	3(3)	-2(3)
C(5)	10(4)	17(4)	10(4)	0(3)	2(3)	-8(3)
C(10)	11(4)	12(3)	11(4)	-2(3)	3(3)	-4(3)
C(12)	12(4)	14(4)	9(3)	-1(3)	-1(3)	-3(3)
C(2)	15(4)	12(4)	7(3)	-1(3)	1(3)	-10(3)
C(15)	8(3)	13(4)	12(3)	1(3)	2(3)	-7(3)
C(1)	15(4)	21(4)	8(3)	-1(3)	0(3)	-4(3)
C(17)	19(4)	24(4)	12(4)	-6(3)	11(3)	-11(4)
C(14)	14(4)	13(4)	10(3)	-1(3)	3(3)	-7(3)

C(9)	16(4)	13(4)	8(3)	-1(3)	-2(3)	-6(3)
C(4)	12(4)	12(3)	6(3)	-2(3)	3(3)	-7(3)
C(7)	11(4)	12(4)	9(3)	-2(3)	2(3)	-8(3)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for MePyrz(TT)$_2$

	x	y	z	U(eq)
H(13A)	7601	6142	3938	14
H(13B)	8374	7851	4122	14
H(6)	-1705	8620	6856	14
H(16A)	8290	10112	1787	12
H(16B)	7627	8383	1582	12
H(5)	-3362	8142	8150	14
H(10)	8041	5865	5402	14
H(12A)	4158	9583	4251	14
H(12B)	3406	7863	4078	14
H(15A)	10546	8186	2801	13
H(15B)	9851	6464	2598	13
H(1A)	5635	2132	10015	23
H(1B)	4259	1160	10684	23
H(1C)	5273	2789	10823	23
H(17A)	10779	8824	766	26
H(17B)	11900	6949	1317	26
H(17C)	12385	8818	1441	26
H(14A)	5651	7985	2852	14
H(14B)	6318	9724	3041	14
H(9)	6684	5359	6729	14

Table S21. Revalent geometric parameters

	Plane to Plane Distances (Å)	Centroid to Centroid Distances (Å)	Additional
Pyrz(FT)$_2$	3.58 (pyrz-furan)	4.74	
Pyrz(TT)$_2$	4.81 (pyrz-thiophene)	--	thiophene-pi 3.22 Å
MePyrz(FT)$_2$	3.60 (pyrz-furan)	5.43	
MePyrz(TT)$_2$	4.48 (thiophene-thiophene)	7.68	

Crystal Maker, OLEX and BIOVIA Discovery Studio Visualizer 2019 was used to explore and identify interactions.